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HIGH ENERGY PROPELLANT INGREDIENT RESEARCH AND DEVELOPMENT

FINAL TECHNICAL REPORT AFRPL - TR - 67 - 37

(1 January 1966 to 31 December 1966)

January 1967

**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA**

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(Prepared under Contract No. AF 64(611) - 11400 by
The Dow Chemical Company,
Midland, Michigan 48540

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FINAL TECHNICAL REPORT (U)
(1 January 1966 - 31 December 1966)

HIGH ENERGY PROPELLANT INGREDIENT
RESEARCH AND DEVELOPMENT (U)

January, 1967

Dow Report Nr. PS-4Q-66

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
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SCIENTIFIC PROJECTS LABORATORY
THE DOW CHEMICAL COMPANY
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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. AP 04(611)-11400. The contract was initiated under Air Force BPSN Nr. 623148, AFSC Project No. 3148, "High Energy Propellant Ingredient Research and Development." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Lt. Robert Bargmeyer as Air Force Project Officer.

This is the final summary report, covering the work performed during the period of 1 January 1966 through 31 December 1966. The Dow report number is PS-42-66.

The aluminum hydride surveillance studies for 1966 are being continued under Contract Nr. FO4611-67-C-0067.

Management direction at Dow is under Dr. R. P. Ruh, Laboratory Director, and the work supervised by Dr. F. M. Brower, Assistant Laboratory Director. Mr. N. E. Matzek is the principal investigator with Mr. R. D. Daniels, Dr. C. B. Roberts, Dr. J. A. Snover, and Mr. E. J. Wilson making major contributions. The assistance of Messrs. D. P. Musinski, H. C. Roehrs, W. Kuehn, J. E. VanPetten, R. L. Williams, F. D. Schmalz in performing many of the experiments discussed in this report is gratefully acknowledged.

Abbreviations used in the text are defined in the Glossary.

This report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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SECTION I

ABSTRACT

(C) Studies of the preparation and properties of AlH_3 -1451 have continued. Magnesium has been incorporated into product made by the continuous crystallization technique; improved thermal stability is observed in product from the larger unit. Flame photometry is used to determine the equivalence point of the AlCl_3 - LiAlH_4 reaction for aluminum hydride synthesis. Teflon PEP showed excellent promise in the laboratory as a material of construction for aluminum hydride crystallization, but adhesion of product still remained a problem in a 9-gallon crystallizer made from PEP stock items. Structure studies of AlH_3 -1451 indicate the decomposition mechanism involves loss of surface hydrogen and formation of aluminum nuclei and anion vacancies. Density measurements of continuous and batch magnesium-doped AlH_3 -1451 show that magnesium forms a substitutional solid solution. The degree of improvement in thermal stability of "aged", magnesium-doped batch samples of AlH_3 -1451 correlates with the initial gassing observed during testing at 60°C. Water, identified as a major component of the gas, plays a major role in the aging process. Heat treatment has increased the stability of some AlH_3 -1451 samples; storing under hydrogen pressure has not. The decomposition rate of standard AlH_3 -1451 in double base propellant at 25°C. became constant at 0.11% per year, requiring 508 days to reach 0.33% decomposition; at 40°C. it reached 0.69% decomposition in 471 days. Double base propellant containing magnesium-doped, in situ DPA-treated AlH_3 -1451 shows a twofold improvement in stability over standard hydride at both 25° and 40°C. Magnesium-doped, in situ DPA-treated, and magnesium-doped, "aged" AlH_3 -1451 are remarkably stable at 60°C. Propellant containing "aged", magnesium-doped AlH_3 -1451 decomposed 0.74% after 243 days. Magnesium-doped, in situ DPA-treated AlH_3 -1451 in double base propellant reached 1% decomposition in 173 days; in composite propellant it reached 0.84% decomposition in 91 days.

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SECTION II

SUMMARY

(C) Studies on the preparation and properties of improved AlH_3 -1451 continued through 1966. Magnesium concentrations up to 2 wt. % were incorporated into product made by the laboratory continuous process, but an increase in stability comparable to that of batch material was not realized. A study of a number of process variables resulted in no improvement in stability. Studies to understand the mechanism by which magnesium stabilizes AlH_3 -1451 and to determine the differences in morphology of the hydride crystals continued.

(C) Work with the continuous crystallizer has concentrated on improving solution stability, eliminating or reducing product adhesion, and incorporating magnesium into the crystal lattice of AlH_3 -1451. The conditions required for direct nucleation of AlH_3 -1451 using the "thermal seeding" technique have been more clearly defined and higher feed rates (2 moles of AlH_3 /hr.) have been successfully used. Three types of decomposition have been recognized, one related to thermal sensitivity of the material and the other two to the presence of impurities. Techniques have been developed to effectively control the rate of decomposition in the crystallizer for periods up to 17 hours.

(C) Magnesium has been incorporated into the crystal lattice of AlH_3 -1451 via the larger scale continuous crystallizer using the complex hydride $\text{LiMg}(\text{AlH}_4)_3$ as the doping agent. Increasing the concentrations of lithium aluminum hydride and lithium borohydride in the feed solution prevented the precipitation of the doping agent at nucleation when the ether concentration is low. Magnesium concentrations greater than one percent were obtained and some, but not all, samples showed improvement in stability; one, containing 1.10% magnesium, required 25 days to reach 1% decomposition.

(U) Polyperfluoroethylenepropylene (FEP) showed excellent promise as a material of construction in the laboratory. Elong runs made in the laboratory 3-liter FEP crystallizer under a wide variety of conditions resulted in excellent nucleation and negligible adhesion and decomposition of product. Less clean-up treatment between runs without loss of product quality was also possible with the FEP-lined vessel.

(C) Successful use of FEP in the laboratory led to the fabrication of a 9-gallon FEP-lined crystallizer. Adhesion remained a problem in the larger scale unit, but the product adhered in the form of "sheets" of AlH_3 -1451 crystals which "flake" after a period of time. This may be due to crystallizer design, agitation, or some other system parameter.

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(C) Laboratory continuous crystallization runs with polytetrafluoroethylene (Teflon TFE) lined vessels indicated that AlH_3 -1451 adhered only to surfaces through which heat was applied. A single run in a pyrex vessel showed the same effect when heat was applied by means of a 400-watt Cio-Quartz pencil-type immersion heater and the bath temperature lowered from 100°C. to 35°C. The result was all AlH_3 -1451 with no sticking on the sides of the pyrex flask.

(C) The optimum conditions required for nucleation of AlH_3 -1451 and for the growth of good crystals are considerably different. It has been proposed that these two stages be separated and that a continuous external nucleator be used to supply AlH_3 -1451 nuclei to a continuous crystallizer unit operated at optimum crystallizing conditions. Preliminary, small-scale laboratory work with this concept has shown encouraging results.

(C) Flame photometry has been used to determine the stoichiometric equivalence point of the aluminum chloride-lithium aluminum hydride reaction, and to determine the amount of excess lithium aluminum hydride in aluminum hydride solutions. The possibility of determining elements other than lithium was investigated by scanning the flame between 3500 and 9000 Å. Only sodium was detectable, if boron and/or magnesium are to be determined, it will be necessary to hydrolyze the sample and obtain the emission spectrum of an aqueous solution.

(C) Structural studies of AlH_3 -1451 indicate that its decomposition mechanism involves the loss of surface hydrogen and the formation of aluminum nuclei and anion vacancies. It is believed that decomposition is initiated at the surface of the crystals, and that, by understanding the mechanism involved, it should be possible to significantly reduce the rate of decomposition of the hydride.

(C) The incorporation of magnesium into the crystal lattice of AlH_3 -1451 greatly increases the thermal stability of batch material, but it has been shown by recent work with the continuous crystallizer that the stabilization of the hydride by this method is not a simple process.

(C) Density measurements of aluminum hydride-1451 obtained from batch and continuous methods indicate the magnesium-doped lattice represents a substitutional solid solution phase. Other factors must be responsible for the variation in stability exhibited by magnesium-doped samples.

(C) Macrocrystalline AlH_3 -1451, surface-treated with diphenylacetylene (DPA), showed a twofold improvement in stability, while magnesium-doped material treated in the same manner showed a fourfold increase. The optimum concentration of the DPA wash solution was established as 2-5 g. DPA/250 ml. of benzene; stability was significantly increased by the in situ treatment with the DPA wash solution.

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(C) The above coating technique did not deposit a sufficient amount of DPA on the surface of AlH_3 -1451 prepared by the continuous process. By using an evaporation technique, whereby a known amount of DPA in an ether solution was dried on the product, controlled amounts of DPA were deposited on the surface.

(C) The mechanism of DPA stabilization of AlH_3 -1451 was investigated. It was shown that no initial chemical reaction between the hydride and DPA occurred, since 85% or more of the DPA deposited by the treatment was removed by a single wash and it was concluded that a weak electronic couple is formed between DPA and AlH_3 -1451; maximum stabilization thus requires a very intimate contact between the DPA and the hydride surface.

(C) A screening program of acetylene derivatives and compounds containing one or more phenyl groups was carried out. Most of the compounds demonstrated some stabilizing effect, but none exceeded the stabilizing effect or lengthening of the induction period of DPA.

(C) Studies were made to understand and characterize the "aging" phenomenon, which is particularly characteristic of magnesium-doped hydrides; the latter exhibited as much as a seven-fold improvement due to the long-term storage. The increase in stability was proportional to the magnesium concentration, with concentration greater than 1.0% necessary for large improvements in stability.

(C) Samples which were removed from -15°C . storage and allowed to stand at ambient temperature for four days showed a considerable decrease in initial gassing and a corresponding loss of stability. Heat treatment of "aged", magnesium-doped aluminum hydride-1451 proved slightly beneficial in improving stability.

(C) The small amount of initial rapid gassing evolved from "aged", magnesium-doped samples at 60°C . was found to correlate roughly with the improvement in thermal stability. Analysis of the gas showed the major constituent to be water vapor, which appears to be playing a major role in the "aging" process. The type of surface structure formed with water in combination with magnesium-doped AlH_3 -1451 must determine the specific conditions necessary for maximum benefit by water treatment of the hydride.

(C) Techniques for accelerating the "aging" of magnesium-doped AlH_3 -1451 were investigated. Water was frozen onto the surface of the hydride at -196°C . and allowed to stand at room temperature before heating at 80° , 70° , 60° , 50° and 40°C . The sample heat treated at 40°C . exhibited the most initial gassing and increase in stability requiring over twice as long to reach 1% decomposition as the standard.

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(C) Macrocrystalline, magnesium-doped and magnesium-doped, DPA-treated AlH_3 -1451 showed no increase in thermal stability when stored under 7,500 psi of hydrogen at ambient temperature for five months.

(U) Cycling the temperature between 70°C. and 90°C. produced approximately the same decomposition curve as that obtained at 80°C. under isothermal conditions.

(U) Additional refinement of the aluminum deuteride-1451 structure was achieved during the past year.

(U) The long-term surveillance of aluminum hydride stored neat and in propellant formulations at -40°C., ambient temperature, and -15°C. continued. These studies showed that significant amounts of decomposition of macrocrystalline AlH_3 -1451 occurred after three months' storage at -40°C. The stability of macrocrystalline samples also steadily decreased in proportion to storage time at -40°C. Magnesium-doped samples decreased initially in stability, but reached a plateau, indicating they may be undergoing an accelerated "aging".

(C) Samples stored at ambient temperature for approximately two years have decomposed less than 1%, while those stored at -15°C. exhibit no decomposition. Recent data indicate that macrocrystalline hydride is much more stable at lower temperatures than originally predicted.

(C) A standard macrocrystalline AlH_3 -1451 sample in double base propellant reached 0.33% decomposition in 508 days at 25°C. After the first 100 days the decomposition rate decreased and remained constant at 0.11% per year. The same sample reached 0.69% decomposition in 471 days at -15°C.

(C) Samples of double base propellant containing improved magnesium-doped and magnesium-doped, in situ DPA-treated aluminum hydride-1451 show approximately a two-fold improvement in stability over standard hydride at 25°C. and -15°C. No decrease in decomposition rate occurred with a surface hydrolyzed sample at -40°C., indicating the stabilizing effect of the double base propellant was ineffective at -40°C.

(C) The slower decomposition rates of AlH_3 -1451 in double base propellant appear to be the result of in situ reaction of the hydride with nitric oxide formed in the decomposition of the propellant.

(C) Magnesium-doped, in situ DPA-treated and magnesium-doped, "aged" aluminum hydride-1451 show remarkable stability in both double base and composite propellant at 60°C., ranging from a two-fold to nearly a tenfold improvement over standard aluminum hydride-1451. The most stable sample contains "aged", magnesium-doped AlH_3 -1451, decomposing only 0.74% after 243 days. A similar

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stability is shown in two magnesium-doped, in situ DPA-treated AlH_3 -1451 propellant samples. One reached 1% decomposition after 173 days in double base propellant and the other reached 0.84% decomposition in 91 days in composite propellant.

(C) Controlled quantities of water added to an AlH_3 -1451 propellant mix appear to have a very significant stabilizing effect. AlH_3 -1451 double base propellant mix to which 0.25% and 0.5% water was added decomposed only 0.54% and 0.46% respectively in 31 days at 60°C.

(C) A single experiment to determine the diffusion rate of hydrogen through double base propellant using radioactive tritium gave a value of $D = 3.85 \times 10^{-4} \text{ cm}^2/\text{hr.}$ at 25°C. and one atmosphere pressure.

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SECTION III

(U) TECHNICAL RESULTS AND DISCUSSION

(C) Research during 1966 has been concentrated on making improved aluminum hydride-1451 by the continuous crystallization process. Every phase of this work has been backed up by laboratory studies to find the best possible techniques and conditions for increasing both the quality and yield of product. A better understanding of the decomposition mechanism has been obtained and stabilizers which markedly increase AlH_3 -1451 stability have been discovered. Long term surveillance studies of AlH_3 -1451 samples have continued and the stability of propellant samples containing improved AlH_3 -1451 has been determined.

A. FUNDAMENTAL CRYSTALLIZATION STUDIES OF ALUMINUM HYDRIDE (U)

(U) Research in the crystallization area during 1966 was oriented toward developing an optimum system for the direct crystallization of AlH_3 -1451. It is expected that a product so obtained will possess improved physical and chemical properties.

1. Laboratory Study of Variables Affecting Crystallization and Stability (U)

(C) Research efforts during the past year have been concentrated on developing a technique for incorporating magnesium into the hydride lattice using the continuous crystallization technique, and on elucidating the process parameters which affect nucleation, growth, product adhesion, and stability of crystalline AlH_3 -1451.

a. Magnesium Incorporation via the Continuous Process (U)

(C) Previous work using the "batch process" showed that the incorporation of small percentages of magnesium into AlH_3 -1451 causes an expansion of the hydride lattice and a substantial increase in its thermal stability. A comparable increase in stability due to the incorporation of magnesium was sought for material made by the continuous crystallization process. Initial work, however, indicated that differences between the two processes existed, and problems such as high chloride concentrations, phase problems, and a reduction in crystallinity would require further study before maximum benefit from magnesium could be realized for the continuous process.

(1) Addition of Magnesium Chloride (U)

(C) Anhydrous magnesium chloride, which had been used successfully in the "batch process", failed to produce satisfactory results when used in the "continuous" process. When it was added to a solution of lithium aluminum hydride prior to aluminum chloride

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addition, no significant amount of magnesium was incorporated into the hydride lattice. By changing the procedure and adding magnesium chloride to a feed solution of complex hydrides having a mole ratio of 1 LiAlH_4 :4 AlH_3 :1 LiBH_4 in a binary solvent consisting of 30% ether and 70% benzene, magnesium was incorporated into the hydride lattice. However, the lithium chloride content of the material produced by this technique increased to 0.3-0.5% and the higher concentrations of lithium aluminum hydride and lithium borohydride required by this method were undesirable in the continuous crystallization process.

(2) Ether-Soluble Magnesium Compounds (U)

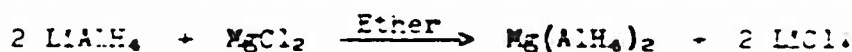
(C) These results indicated that a more desirable magnesium compound would be one which was ether-soluble and contained no chloride or other elements which would interfere with the incorporation of magnesium into the AlH_3 -1-51 lattice.

(a) Reaction Product of Lithium Aluminum Hydride and a Grignard Reagent (U)

(U) An attempt was made to prepare an ether-soluble magnesium compound by reacting a Grignard reagent with lithium aluminum hydride; it was believed that a compound with a general structure of RMgAlH_4 would be obtained. Approximately 25% of the lithium aluminum hydride solution was added to the Grignard reagent before precipitation occurred, and upon completion of the reaction it was found that only 50% of the theoretical amount of lithium chloride was recovered. This solution, when added to an aluminum hydride feed solution, delayed nucleation, created phase problems, and produced material of poor crystallinity.

(b) Lithium Magnesium Aluminum Hydride (U)

(U) The reaction between magnesium chloride and lithium aluminum hydride was originally believed to proceed as follows:



with the resulting magnesium aluminum hydride producing the increased stability observed in the "batch" process. Laboratory studies showed, however, that the above reaction proceeded to only 70-80% completion when a 25% excess of lithium aluminum hydride was used, and while the soluble chloride concentration varied, it usually remained below a mole ratio of 1 Cl:1 Mg. Further experiments showed that the chloride concentrations of the above ether solutions could be decreased approximately 5% by treatment with sodium borohydride. Sodium aluminum hydride was even more effective, reducing chloride concentrations to levels which can be tolerated (0.01 M). It is necessary, however, when treating the solutions with sodium aluminum hydride, to keep the magnesium concentration below 0.2 M to prevent the product from precipitating.

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(U) The excess concentration of lithium aluminum hydride also varied, depending upon the degree of completion of the reaction, and was usually greater than a mole ratio of 1 Li:1 Mg. This excess lithium could not be removed from solution by reaction with aluminum chloride, indicating that it was present as part of a discrete chemical compound other than lithium aluminum hydride. Removal of ether from the solution yielded a single crystalline phase in the form of clear, irregular plates, usually clustered together. Elemental analysis supports the formula $\text{LiMg}(\text{AlH}_4)_3$. The novel X-ray diffraction powder data giving the "d" distances and relative intensities are shown in Table I. The infrared absorption spectrum of the new phase compared with the spectra obtained from magnesium aluminum hydride and lithium aluminum hydride is shown in Figure 1.

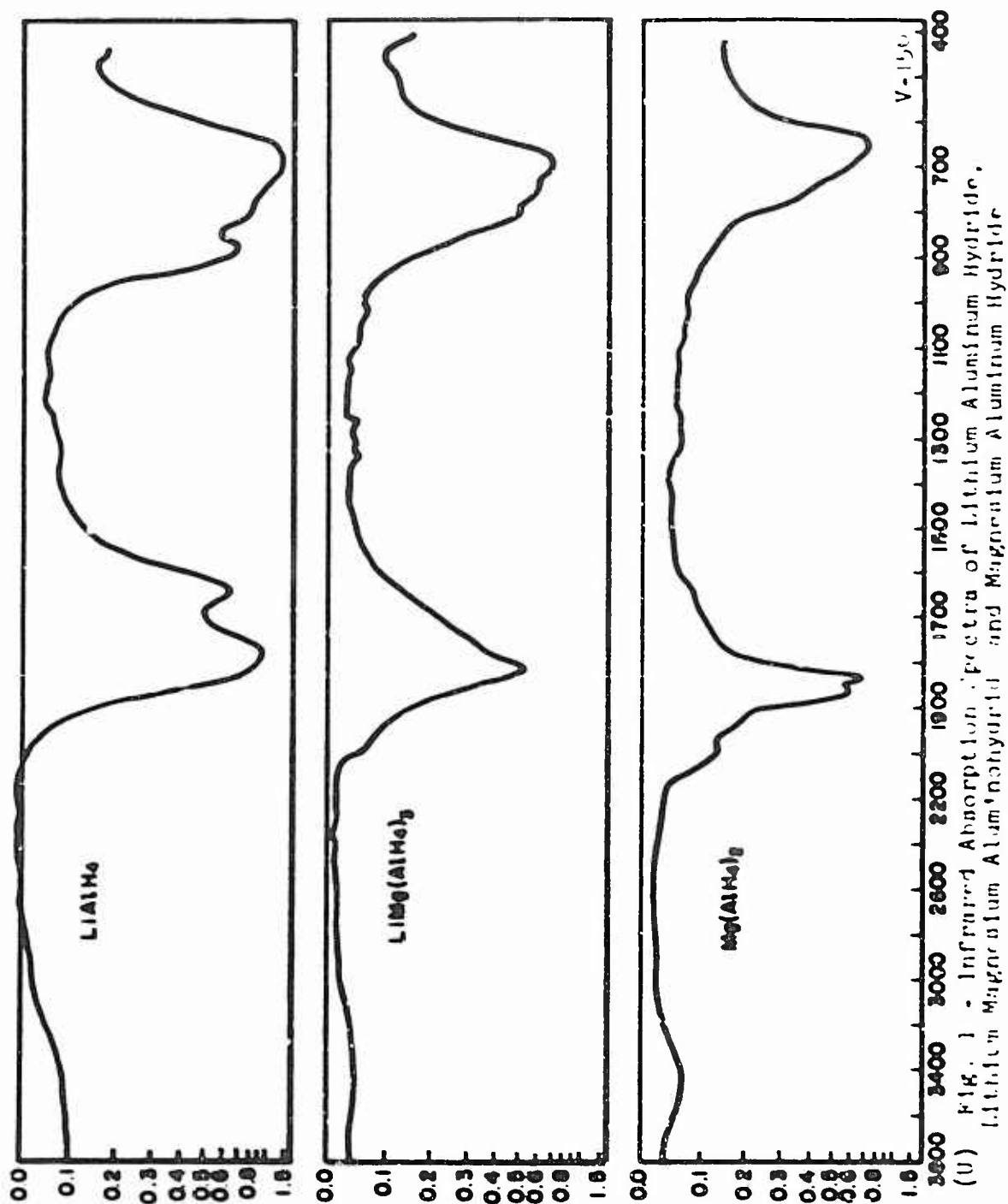
Table I

(U) X-Ray Powder Diffraction Data
for Lithium Magnesium Aluminumhydride

d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
7.0	15	2.50	30	1.87	20	1.447	3
5.9	20	2.45	50	1.85	8	1.431	2
5.4	30	2.41	15	1.79	8	1.420	2
4.11	50	2.40	4	1.76	10	1.398	2
3.80	80	2.35	15	1.73	4	1.375	5
3.70	30	2.31	4	1.69	3	1.350	2
3.60	50	2.26	6	1.67	3	1.339	4
3.53	100	2.22	13	1.64	6	1.315	4
3.30	30	2.19	13	1.63	3	1.255	5
3.25	50	2.09	30	1.60	8	1.240	4
3.04	50	2.05	10	1.58	6	1.195	2
2.78	20	2.01	20	1.56	2	1.115	2
2.74	13	1.99	4	1.51	15	1.105	2
2.68	40	1.96	10	1.467	7	1.091	3
2.64	6	1.91	6				

(C) Magnesium can be incorporated into the crystal lattice of AlH_3 -1451 through the use of $\text{LiMg}(\text{AlH}_4)_3$ solutions. However, the use of these solutions produces some difficulties with nucleation and crystal growth, especially when concentrations of magnesium greater than 1% are incorporated into the hydride lattice. These problems can be resolved by the use of higher concentrations of lithium aluminum hydride and lithium borohydride in the crystallizing solution. Using this technique, a maximum

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(U) FIG. 1 - Infrared Absorption Spectra of Lithium Aluminum Hydride, Lithium Magnesium Aluminum Hydride and Magnesium Aluminum Hydride

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concentration of 2.3 wt. % magnesium has been incorporated into the hydride lattice via the continuous process. Higher concentrations of the complex hydrides, lithium aluminum hydride and lithium borohydride, apparently increase the solubility of the lithium magnesium aluminohydride, preventing its precipitation as $\text{LiMg}(\text{AlH}_4)_3$ during crystallization, but they also cause more agglomeration and product adhesion to the walls of the vessel during crystallization.

(c) Lithium Magnesium Borohydride (U)

(C) Lithium magnesium borohydride, $\text{LiMg}(\text{BH}_4)_3$, was prepared for the purpose of examining its use as an alternate material for the incorporation of magnesium into the hydride lattice. This borohydride complex is much more soluble than $\text{LiMg}(\text{AlH}_4)_3$ in the ether-benzene solvent system. However, the presence of lithium aluminum hydride in the crystallizing solution appears to cause an exchange reaction, as shown below,



because platelets of $\text{LiMg}(\text{AlH}_4)_3$ are still observed during crystallization. Hence, the incorporation of magnesium into the hydride lattice via the continuous process is not improved by the use of the analogous borohydride compound.

b. Stability Studies of Magnesium-doped Aluminum Hydride-1451 Produced by the Laboratory Continuous Process Method (C)

(C) The soluble magnesium solutions used for the continuous process can be used for the batch process, and the resulting product exhibits the usual increase in thermal stability. However, laboratory samples prepared via the continuous process with comparable amounts of magnesium have not generally shown so significant an improvement. The reason for this is not fully understood at present, although previous experience indicates that with continued effort this condition can be corrected. The laboratory continuous process is similar to that used in some earlier Dow work in which the feed to the crystallizer contained relatively large amounts of lithium aluminum hydride and lithium borohydride. In this study, initial difficulties were also encountered, but ultimately magnesium was incorporated into AlH_3 -1451 and an increase in stability was achieved.

(C) It appears that minor differences in process techniques can be responsible for significant differences in product stability where magnesium incorporation is involved. Efforts to modify procedures and obtain more stable material from the larger scale continuous process have resulted in several runs which show that an improvement in stability is being realized.

(C) Elemental analyses of laboratory samples show a magnesium concentration up to 2 wt. %, and X-ray diffraction shows the

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characteristic lattice expansion. These data indicate that the incorporation of magnesium into the crystal lattice is similar for both processes. The difference in thermal stability, however, suggests that other parameters are playing an important role in the stabilization of magnesium-doped AlH_3 -1451. The following variables have been investigated in the laboratory in attempts to improve the stability of magnesium-doped material prepared via the continuous process:

- (i) Residence time in the hot crystallizing solution.
- (ii) Chloride content of the product.
- (iii) Additive hydride (LiAlH_4 and LiBH_4) ratios and/or concentrations.
- (iv) Use of $\text{LiMg}(\text{AlH}_4)_3$ solutions or direct addition of MgCl_2 .
- (v) Particle size.

Changing these variables has produced no significant change in the thermal stability of the AlH_3 -1451 product (Table II); other reasons were therefore investigated.

(C) Previous data have indicated that dry box atmospheres containing small amounts of water (250. ppm) have increased the stability of magnesium-doped AlH_3 -1451 prepared via the batch process (1). The improvement in stability was attributed mainly to surface hydrolysis and/or oxidation. A wet ether wash treatment of a batch sample and two continuous magnesium-doped samples imparted no further stability to the product.

(C) Wet ether for the reaction solutions was also used to make magnesium-doped AlH_3 -1451 via the continuous process, and, as with the wet ether wash, no improvement in product stability resulted. Surprisingly, neither AlH_3 -1563 and/or AlH_3 -1717, usually associated with water, were not observed.

(C) The above experiments again point out the sensitivity of this system to small variations in procedure. The presence of moisture will not always produce certain aluminum hydride polymorphs or give more stable product unless it is introduced by the proper technique.

(C) One of the significant differences between the "batch" and "continuous" product is the particle size and crystallinity. The continuous process usually results in larger and more crystalline particles. Assuming that the stabilization of AlH_3 -1451 is a surface phenomenon, consideration of this difference would suggest that the greater the surface area of magnesium-doped hydride, the greater the thermal stability.

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Table II
(C) Parameter Effects on Continuous Process Aluminum Hydride-1421

Run No.	Process	% Mg	% DPA ^a	Stability Days to 1% at 60°C.		Treatment
				Control	Treated	
137	Batch	1.90	---	24	25	1000 ppm H ₂ O in ether wash
131	Continuous	0	---	8.5	7.5	1000 ppm H ₂ O in ether wash
136	Continuous	1.70	---	5	4.5	1000 ppm H ₂ O in ether wash
147	Continuous	1.54	---	6.5	---	2 mmoles H ₂ O in ether
148	Continuous	1.62	---	7.0	---	8 mmoles in reaction
130	Fine Powder	<0.1	---	4.75	---	
135	Fine Powder	1.56	---	4.0	---	
140	Cont. at 76.5°C.	1.35	---	3.2	---	Conversion thru 1433 phase
142	Cont. at 77.5°C.	0.75	---	8.3	---	Conversion thru 1433 phase
134	Batch	0	0.8	(5-6) Av.	12.5	DPA wash treatment
67	Batch	1.42	---	14	---	No DPA
62	Batch	1.6	0.8	81	---	DPA wash treatment
74	Continuous	0	0.4	8	7	DPA wash treatment
79	Continuous	2.05	0.6	5	5	DPA wash treatment
92	Continuous	1.54	4.92	6.25	13	DPA dried on product
99	Continuous	1.60	1.60	5.5	8	DPA dried on product
100	Continuous	0	1.63	6.0	11	DPA dried on product
127	Continuous (PEP) ^b	0	1.95	7.0	15.5	DPA dried on product
129	Continuous (PEP)	0	3.24	5.5	9.75	DPA dried on product

^aDiphenylacetylene.

^bPerfluoroethylenepropylene copolymer liner.

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(C) In order to test this hypothesis, the stability of magnesium-doped samples of hydride prepared by the "fine powder" process was evaluated. The particle size is generally 1-5 μ compared to $\sim 50 \mu$ for batch material. The incorporation of magnesium into the fine powder material failed to show any improvement over standard fine powder as shown in Table II. This indicates magnesium stabilization is not a function of surface area or particle size.

(C) Another significant difference between the batch and continuous process is the mode of preparation. Aluminum hydride in the batch process separates first as an amorphous or possibly liquid phase, crystallizes as an aluminum hydride etherate-1443 phase, then desolvates to AlH_3 -1433 before undergoing a solid state transformation to AlH_3 -1451. In the continuous process with the thermal seeding technique, aluminum hydride has been observed to nucleate and grow directly from solution as AlH_3 -1451. It is possible that a phase conversion sequence occurs in a thin layer on the surface of the AlH_3 -1451 crystals, but this has not been observed microscopically.

(C) Several attempts to produce magnesium-doped AlH_3 -1451 via the continuous process by first crystallizing AlH_3 -1433 resulted in only two successful runs; due to the high aluminum hydride concentrations, AlH_3 -1444 was usually produced. These two runs, however, did not show any improvement in stability as seen in Table II. This would suggest that the solid state which involves the transition of AlH_3 -1433 to AlH_3 -1451 is not the controlling factor in magnesium stabilization.

(C) This conclusion is also supported by the results obtained from the magnesium-doped, fine powder material. Samples of AlH_3 -1451 prepared by this process are known to undergo this solid state transformation. However, no improvement in stability was observed. The results show that the incorporation of magnesium into the crystal lattice will produce a more stable product in only one of three related processes. No improvement is obtained if the sample is prepared via the "fine powder" or "lab continuous" process, but this stabilization technique is very effective if used in the "batch" process. This dictates, therefore, that continued efforts be made to understand the mechanism by which magnesium stabilizes AlH_3 -1451.

c. DPA-Treatment of Samples Prepared via the Continuous Process (C)

(C) The diphenylacetylene (DPA) wash treatment successfully applied to batch material did not deposit a sufficient amount on the surface of AlH_3 -1451 prepared via the continuous process. However, by using an evaporation technique, whereby a known amount of an ether solution of DPA was dried on the product, controlled amounts of DPA can be deposited on the surface.

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(C) Using this technique, the stability of laboratory samples prepared by the continuous process was increased approximately two-fold as shown in Table II. These samples reached 1% decomposition in 8-16 days at 60°C. This stability is not as spectacular as that achieved in batch, magnesium-doped, in situ DPA-treated samples which require 50-60 days before reaching 1% decomposition at the same temperature (see Section B.3.a.).

d. Nucleation Studies (U)

(C) Studies on the direct crystallization of aluminum hydride have shown that one of the most important controlling factors in producing good crystalline AlH_3 -1-51 by the continuous crystallization process is the initial nucleation stage. Repeated experiments have demonstrated it is not possible to seed this crystallization. As a result, it is necessary to conform to a very narrow set of operating conditions to obtain in situ nucleation of the AlH_3 -1-51. These conditions are defined as follows:

- (i) A temperature of 79°-80°C., corresponding to less than 1% diethyl ether.
- (ii) An aluminum hydride concentration of approximately 0.005 M, but never greater than 0.010 M.
- (iii) A slow feed rate of 0.1-0.2 moles/min./l. (The feed rate can be increased during crystal growth, but not during the initial nucleation).
- (iv) Complex hydride mole ratios of $LiAlH_4:AlH_3:LiH_2$ within the range 1:4:1 to 1:10:1.
- (v) The use of very low concentrations of lithium aluminum hydride and lithium borohydride to prevent precipitation during the nucleation stage and the resulting detrimental effect upon subsequent crystal growth.

(U) Extensive studies with variables such as feed rates, aluminum hydride concentration, lithium aluminum hydride concentration, ether concentration, and time and temperature profiles have not given a completely reproducible nucleation technique. This variability is believed to be due to unknown impurities such as lithium chloride, water and/or reaction products of water, and additives like magnesium inhibiting the nucleation stage. These impurities are perhaps more difficult to establish, but, once defined, they are also amenable to control. Trace impurities in the solvents, especially in recycle benzene, have been found to cause variations in nucleation and the resulting crystal phase.

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e. Crystal Growth Studies (U)

(C) Feed rates in the nucleation stage must be extremely slow; however, once nucleation has occurred, it is possible and desirable to substantially increase the feed rate to lower the boiling point of the crystallizing solution to 76°-77°C. and reduce the residence time of the AlH_3 -1451 crystals in the crystallizer. It has been observed that slow feed rates during the growth stage result in the production of more opaque and polycrystalline material than faster feed rates. A slight improvement in the thermal stability of the hydride is also noted because of the shorter residence time of the hydride particles in the crystallizer.

(1) The Effect of Lithium Aluminum Hydride on Crystal Growth (U)

(C) Precipitation of lithium aluminum hydride during the crystal growth stage will also cause the hydride crystals to become more opaque and polycrystalline. Thus, it is necessary in obtaining maximum crystallinity to keep the concentration of lithium aluminum hydride as low as possible in the feed solution without introducing chlorides to the system.

(2) Quaternary Ammonium Aluminum Hydride as a New Desolvating Agent (U)

(C) One method of eliminating the precipitation of lithium aluminum hydride during crystallization of AlH_3 -1451 would be to use a more soluble aluminohydride as a desolvating agent. Tri-n-octyl n-propyl quaternary ammonium aluminum hydride (R_4NAlH_4) was synthesized from the corresponding quaternary bromide salt and lithium aluminum hydride in benzene. This solution was then used to crystallize a stoichiometric hydride feed solution via the continuous process. There was a considerable delay in the nucleation of the aluminum hydride, after which AlH_3 -1433, AlH_3 -1451, and a trace amount of AlH_3 -1444 crystallized. Although no lithium aluminum hydride or R_4NAlH_4 precipitated, nucleation and phase problems were obvious, and no further work was done with this type of compound.

f. External Nucleation (U)

(C) The optimum conditions required for nucleation of AlH_3 -1451 and for the growth of good crystals are considerably different. Therefore, it has been proposed that these two stages be separated, and that a continuous external nucleator be used to supply AlH_3 -1451 nuclei to a continuous crystallizer unit operated at optimum crystallizing conditions. Preliminary, small scale laboratory work with this concept has shown some encouraging results.

(C) The first system to be studied consisted of a heated chamber where metered streams of 0.05 M AlH_3 solution (~94% benzene

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-10% ether) and preheated benzene were mixed. A metering pump, which controlled the flow rate of both streams, was connected to the chamber by means of 1/8" Teflon tubing. The mixing chamber and exit tube and the flow rates of the feed streams were varied. The residence time of the feed solution in the hot zone was calculated from the volume and feed rates to be between one and ten minutes.

(C) This system produced $\text{AlH}_3\text{-I}^{451}$ in all runs, but the yield was lower than expected. Some crystals were 20-30 μ in diameter, which suggested that this method might also be developed into a crystallizer to produce microcrystalline $\text{AlH}_3\text{-I}^{451}$. The advantage of a very short residence time in the hot zone should result in material of improved stability. When faster feed rates were used, some $\text{AlH}_3\text{-I}^{433}$ and $\text{AlH}_3\text{-I}^{444}$ were also produced.

(C) Exact control of this small-scale system was difficult and two major problems were encountered. First, vaporization of the ether in the heated tube caused bubbling and separation of the solution, with the resulting expansion of ether vapor decreasing the residence time in the chamber. The second problem was product adhesion which caused material to build up in the narrow tubes, eventually plugging them.

(C) A second system consisted of feeding the mixed feed streams into the middle of a vertical glass tube and removing the ether at the top by means of a distillation column. The product was drawn off the bottom by a gravity overflow system which functioned erratically and produced large liquid level changes in the vertical glass tube; product adhesion also plugged the narrow overflow tubes. Despite these problems, $\text{AlH}_3\text{-I}^{451}$ was produced in the system.

(C) A modification of the above procedure was also studied. All liquids pumped into the system were taken off by distillation and product was intermittently removed through a stopcock in the bottom. Several runs produced $\text{AlH}_3\text{-I}^{451}$ and $\text{AlH}_3\text{-I}^{433}$ which settled out readily and resulted in an increase in retention time compared to the Teflon tube system.

(C) The above preliminary work has shown that a continuous external nucleator can be developed to aid in the continuous crystallization of $\text{AlH}_3\text{-I}^{451}$. However, more development work will be necessary to produce a working model and establish controlling parameters.

g. Materials of Construction (U)

(U) The random nature of decomposition observed during batch runs in pyrex glass as well as adhesion to the surfaces suggested that some other material of construction might either reduce or eliminate these problems.

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(1) Quartz, Vycor and Soft Glass (U)

(C) Experiments with a quartz thermometer well showed a significant improvement in the amount of decomposition of aluminum hydride over pyrex thermometer wells. Although the striations were more pronounced on the quartz well, no aluminum coating formed, as it did with pyrex. In order to further investigate this difference, a one-liter quartz flask with a quartz thermometer well was fabricated, and a series of runs made using this vessel for desolvation of aluminum hydride.

(C) Six batches of aluminum hydride-1451 were made in the quartz flask, and the previous observation was confirmed; no metallic aluminum coating was observed on either the thermometer well or sides of the flask in any of the runs. Little improvement, however, was noted in the amount of product adhering to the sides of the flask, and, as with pyrex, a gradual coloring of the material occurred as temperature was maintained at 70°C. These results indicate two types of decomposition which occur during the conversion step. The first is catalytic and the degree to which this type of decomposition occurs depends upon the surface in contact with the solution. This type of decomposition generally results in a coating of metallic aluminum which deposits in a random manner on the surface of the container. Of four materials tested - soft glass, vycor, pyrex, and quartz - the latter was the only one exhibiting a complete absence of this type of decomposition. Soft glass and vycor produced aluminum coatings, while pyrex showed random deposition of aluminum on both the sides of the flask and the thermometer well. The second type is a thermal decomposition of the aluminum hydride which occurs at the surface of the flask where the product adheres. This occurred with all the above materials and none appeared to have an advantage in this respect.

(U) This work suggested the use of an entirely different type of material, such as polymers with highly non-adhesive surfaces. Polyperfluorooethylenepropylene (FEP) polymer appeared to be the most promising and exhibited excellent non-adhesiveness (see Section A.1.h.).

(2) Titanium Metal (U)

(C) Further work was carried out toward the end of 1966 on determining the use of metals as materials of construction. Titanium is a relatively inert element, being resistant to both caustic and concentrated hydrochloric. Its effect upon the decomposition and/or adherence of aluminum hydride was not known, and in order to determine this a two-liter crystallizing vessel was fabricated. Two runs using the drip-in procedure resulted in AlH_3 -1451, but decomposition and adhesion were observed in both cases. These results indicate that titanium metal is not a suitable material of construction for a crystallizer. A tantalum vessel has been ordered, and its properties as a material of construction should be determined.

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h. Product Adhesion (U)

(C) Product adhesion on the walls of the continuous crystallizer presents a very critical problem, since it results in a significant loss of product and very low yields. In addition, if the product is maintained near or at the heated surface of the vessel wall, it will be only a matter of time before decomposition of this product occurs, requiring a shut-down and clean-up of the crystallization unit. Solution of this problem would result in increased yields, longer run times, and reduced clean-up efforts.

(1) The Effect of Additive Hydrides (U)

(C) Experience indicates that the precipitation of lithium aluminum hydride before, during, or after nucleation of AlH_3 -1451 accentuates the adhesion problem. Rapid nucleation of AlH_3 -1433 due to AlH_3 concentrations greater than 0.005 M also results in excessive product adhesion. Varying the concentrations and ratios of the complex hydrides, lithium aluminum hydride and lithium borohydride, has not solved this problem, although higher lithium borohydride concentrations aid in solubilizing the lithium aluminum hydride and the magnesium compound, $\text{LiMg}(\text{AlH}_4)_3$. The precipitation of lithium aluminum hydride is particularly prevalent in the temperature range of 75°-80°C. If too high a concentration of lithium borohydride is used, it will also precipitate under these conditions.

(2) Ultrasonic Agitation (U)

(U) An immersion type ultrasonic transducer was used for agitation of the benzene solution during three continuous crystallization runs. Although the generation of a larger number of nuclei by this technique was expected, no significant effects were observed. However, no product adhesion to the glass crystallization flask occurred during these runs, while a control run with the same feed and normal stirring did result in product adhesion. Therefore, the use of ultrasonics for solving the adhesion problem looks promising.

(3) The Use of Polyperfluoroethylene-propylene Copolymer (Teflon PEP) as a Material of Construction (U)

(C) Previous work with flasks made from various materials showed a wide variation in the amount of catalytic decomposition of aluminum hydride. Of these, quartz resulted in the least amount of catalytic decomposition, but a serious adhesion problem still remained (see Section A.1.g.). Efforts to find materials which are both non-catalytic and non-adhesive were therefore continued.

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(C) A 500 ml. polypropylene Erlenmeyer flask was fitted with an adapter and used as a crystallization vessel. The product of two runs was AlR_3 -1-33, but it was observed that adhesion of product to the sides of the flask was reduced and the material remained white. Some softening of the polypropylene in the heating bath (100°C.) was observed.

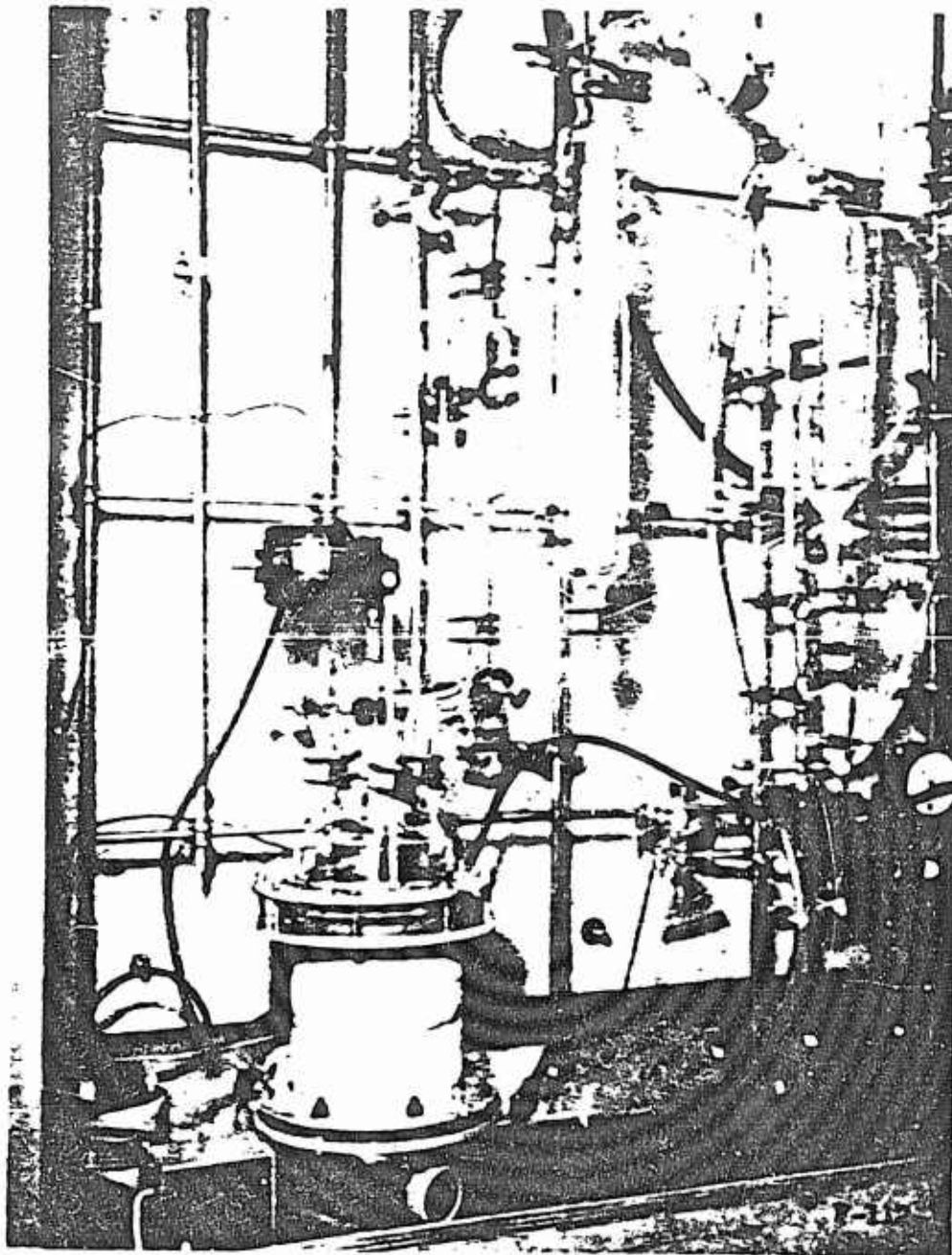
(C) Polyperfluoroethylenepropylene copolymer (Teflon FEP) has more desirable properties than polypropylene. It is inert to organic solvents, non-porous, has excellent adhesion resistance, and can withstand temperatures up to 205°C. In order to study its effect upon AlR_3 -1-51, a 32-ounce Teflon FEP bottle was fitted with a glass adapter and a thermocouple well. No stirring other than that resulting from the boiling of the solvent was provided.

(C) The results from eight runs using the FEP vessel and the batch method indicated that it is superior to any other material of construction previously used. A small amount of sticking of product occurred soon after precipitation, but most of the sticking disappeared as crystallization proceeded. Decomposition was considerably reduced and the product, AlR_3 -1-51, remained white after three hours of refluxing. The pyrex thermocouple well, although not a heated surface, always exhibited more adhered product and decomposition than the walls of the container. The small amount of material which adhered to the sides of the flask was easily loosened at the conclusion of the run by swirling the solvent, suggesting that better agitation probably would have prevented it from sticking initially. Successive runs could also be made in the same bottle with only a benzene rinse required for clean-up. This is in marked contrast to pyrex which has always required an acid-base treatment between runs.

(U) The Teflon FEP bottle employed for the batch process was not useful for the continuous process and it was therefore necessary to design an FEP-lined vessel which could be fitted with the proper outlets at the top. The bottom of a piece of FEP-lined pipe six inches in diameter and eight inches long was sealed by means of an FEP sheet (0.090 inch thick) held firmly against the pipe liner by means of a 1/4" aluminum plate and a split flange. A glass top with three female 35/25 call joints and a thermometer well was fitted with a gasket and a second split flange to provide a vapor-tight seal. Agitation was provided by a Teflon (TFE) paddle (approximately 200 rpm) and the solution was heated by a 700 watt electric tape wrapped around the outside of the pipe. The vessel, shown in Figure 2, holds approximately three liters and is comparable in operation to the pyrex vessels previously used for this purpose.

(C) The objective in fabricating the vessel was to evaluate this material of construction for compatibility and product adhesion resistance properties during continuous crystal-

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(1) Fig. 1 - Photograph of T-Flon FEP Vessel

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lization. The initial work was done in a clear Teflon FEP bottle. However, because green commercial FEP contains a small amount of Cr_2O_3 , an evaluation of the commercial resin was necessary to determine if the Cr_2O_3 would increase the decomposition of the hydride; Teflon FEP can also be obtained without the chromic oxide.

(C) A number of runs made with this vessel confirmed the previous results obtained by the batch process. There was little or no product adhesion below the liquid level although some build-up was noted above the liquid level, probably a result of solution evaporating from the hot surface. These deposits were easily removed by flushing, but did not appear to be removed by simple agitation of the solution. The glass thermometer well showed the usual streaking, product adhesion, and some decomposition; the Teflon TFE stirrer blade was also heavily coated with product. High ratios of additive hydrides, the precipitation of AlH_3 -1-33, and the addition of the magnesium solution did not increase the amount of adhered product on this vessel.

(U) A decrease in the length of time required for clean-up between runs was also indicated. Two runs were made without the usual clean-up treatment with acid, base and water after the preceding run. In both cases, the product was of good quality and no difficulties due to decomposition or adhesion were observed.

(C) The results from eight runs tabulated in Table III show that commercial FEP, either green or colorless, is a superior material of construction for AlH_3 -1-31 processing. These conclusions led to the construction of a nine-gallon, FEP-lined unit for further developmental studies of the continuous crystallization (see Section III.B.4).

(4) The Use of Polytetrafluoroethylene (TFE) as a Crystallizing Vessel Liner (U)

(U) The excellent properties shown by the three-liter FEP-lined laboratory crystallizer were not realized in the nine-gallon continuous vessel. Adhesion remained a problem in the latter case, although the product adhered much more loosely than with either glass or Haresite. In addition, a serious heat transfer problem was encountered, principally because the Teflon FEP was not bonded to the metal container.

(U) Previous experience with polytetrafluoroethylene (TFE) in the form of coated stirring bars, stirrers, etc. had indicated that a reduction in adhesion would not result from the use of this material. However, these were machined surfaces, and adhesion could have been due to a relatively rough surface. The minor differences in chemical composition between Teflon FEP and Teflon TFE indicated a more thorough study of the latter

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Table III
(U) Summary of Preparations in an PEP-Lined Vessel

Run No.	Hydride Ratio of 1st and 2nd Feed ^a	Time hours	Product Adhesion	Stability, days at 1% Decomp. at 60°C.	Comments
1	1:4:1 throughout	2.0	Very slight	5.5	Adhesion and decomp. on stirrer and thermo. well.
2	1:6.7:0 + 0:1:0	4.0		8.0	Not opened or cleaned.
2a	Solution from run No. 2 + 0:1:0	3.0	Slight	---	Trace AlH ₃ -1444 observed.
3	1:10:1.5 + 0:1:0	4.0	None	5.0	Trace decomposition in run; not in product.
4	1:10:0 + 0:1:0	3.5	Trace	6.0	Feed feed; AlH ₃ -1453 phase.
5	1:10:1 + 0:1:0 ^b	3.5	None	6.0	---
6	1:10:1 + 0:1:0 ^b	4.8	None	4.75	Incorporated 1.36% Mg.
7	1:4:1 + 0:1:0	4.0		7.0, 15.5 (DPA)	Product split; one-half DPA-treated (2%).
8	1:4:1 + 0:1:0	3.75	Trace	5.5, 9.75 (DPA)	Product split; one-half DPA-treated (2%).

^aRatio of LiAlH₄: AlH₃: LiBH₄ - 100 mmole AlH₃ each feed.
^bTwo 0:1:0 feed solutions added.

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should be made, particularly since it can be readily bonded to metal and, therefore, provides good heat transfer.

(C) Teflon TFE-lined kitchen utensil pans were used for this work employing the same glass top as previously described. The first pan, which had a te-colored coating, was heated by means of a hot plate and a small heating tape wrapped around the sides. The temperature between the hot plate and the pan was maintained at 24°C. by means of a temperature controller, while a variac setting of 15 was used to heat the tape. A single batch run produced excessive sticking of $\text{AlH}_3\text{-l-51}$, particularly on the bottom of the pan where the heat was applied; no adhesion was noted on the sides.

(D) The second pan which had a black, and supposedly more durable coating, was heated by means of the tape only, with a variac setting of 50-55. A drip-in run produced only $\text{AlH}_3\text{-l-51}$ with no adhesion to the vessel surface. After cleaning with acetone and cold, a second run was made with a variac setting of 15 and in this case considerable adhesion occurred on the sides of the pan where it was heated, but none on the bottom.

(E) The results from these three runs indicated that adhesion occurred only on the heated TFE surfaces, and, when this was reduced, as in the second run (variac setting 50-55) no adhesion occurred.

(F) The Effect of Wall Temperature on Aluminum Hydride-l-51 Adhesion to Pyrex Glass (C)

(C) Product adhesion to pyrex glass has always been a serious problem. To determine the effect of temperature on this material, a regular drip-in run was made, but the method of heating the ether-benzene solvent was changed. The silicone oil bath temperature was reduced from the usual 100°C. to 85°C. The remainder of the heat was supplied by a 400-watt Glo-Quartz pencil-type immersion heater placed in the thermometer well which extended two to two and a half inches below the surface of the solvent. The result was all $\text{AlH}_3\text{-l-51}$ with no sticking on the sides of the pyrex flask. The thermometer well which heated the solution did become coated, although the amount of adhered material was comparatively small.

(D) Considerably more adhesion would normally be expected on the sides of the flask with a bath temperature of 100°C. It must be concluded, therefore, that the wall temperature of the crystallizer vessel is an important factor in adhesion, and that it should be kept as low as possible. Differences in design and the resulting internal wall temperature may explain why adhesion remains a problem in the nine-gallon FEP-lined crystallizer and not in the smaller laboratory models.

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1. Flame Photometry Studies of Aluminum Hydride Solutions (U)

(U) The determination of alkali metals in a non-aqueous solvent is a known analytical technique. It therefore appeared feasible to determine lithium and sodium in ether-benzene solutions of aluminum hydride, and to use this information for more precise control of the crystallization process.

(1) Determination of Exact Stoichiometry for Preparation of Aluminum Hydride (U)

(C) With the continuous crystallization technique it is extremely important to know the exact stoichiometric equivalence point of the aluminum chloride-lithium aluminum hydride reaction. If excess aluminum chloride is present, the run will not nucleate; if a large excess of lithium aluminum hydride is present, the product adheres to the wall of the crystallizer.

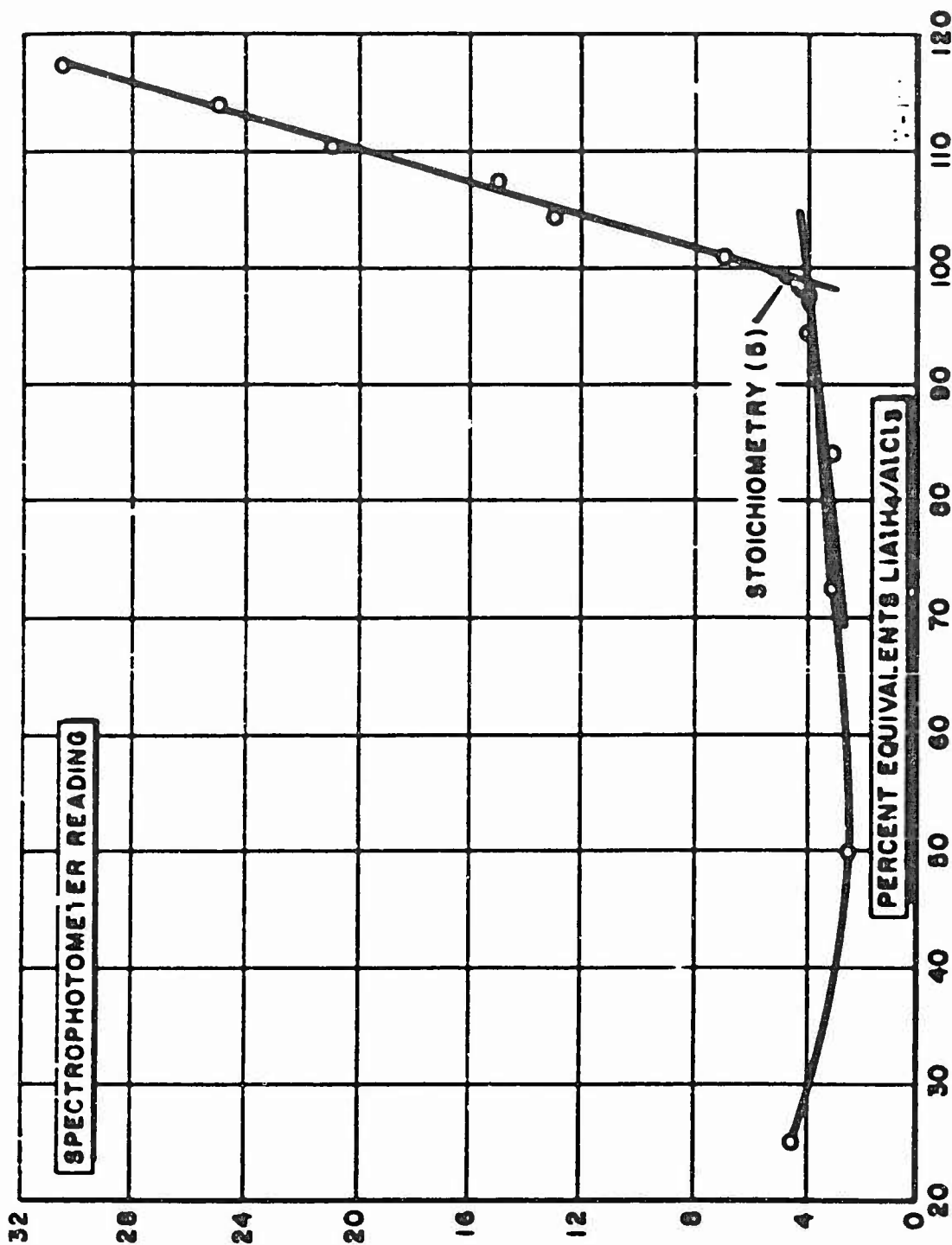
(C) This problem was solved by the application of flame photometry to the analysis of aluminum hydride solutions. When lithium aluminum hydride is added to aluminum chloride, only the solubility of lithium chloride is responsible for lithium concentration up to the stoichiometric equivalence point. Beyond this, an excess of lithium aluminum hydride appears, and lithium concentration increases rapidly. The change in lithium concentration can be followed by measuring the emission of the 6708 Å lithium line. It remains practically constant until the stoichiometric equivalence point, after which it abruptly rises.

(U) A linear relationship of emission versus concentration is obtained for lithium aluminum hydride solutions up to about 0.2 millimolar, a concentration which requires approximately a thousandfold dilution of the aluminum hydride feed sample. This is readily accomplished by mixing 0.050 ml. of aluminum hydride solution with 50 ml. of tetrahydrofuran in a 60 ml. serum bottle, producing the proper concentration range to provide a spectrophotometric response for lithium in the linear portion of the emission curve, to prevent precipitation of aluminum hydride, and to eliminate plugging of the flame jet in the instrument.

(U) Figure 3 shows the flame emission of lithium at 6708 Å for standard reaction mixtures ranging from 25 to 117 percent of stoichiometry. The intersection of a straight line resulting from a small amount of soluble lithium chloride in the presence of aluminum chloride and another straight line due to the presence of excess lithium aluminum hydride establishes the equivalence point with an estimated accuracy of $\pm 0.5\%$. It can be seen, therefore, that an aluminum hydride solution which provides an emission reading of less than 5 is on the aluminum chloride side, and, as a result, will not nucleate properly. Readings higher than 5 can be used to calculate the amount of excess lithium aluminum hydride. This analysis has resulted in much closer control of the crystallizer feed solution composition.

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(11) Fig. 2 - Plane Reduction of Lithium for Standard AlCl_3 - LiAlH_4 Mixture

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(U) Convenient and rapid sampling techniques and standardized procedures for sample preparation and analysis of aluminum hydride solutions have been worked out. Figure 4 shows the three-way sample valve being used with the flame photometer. A standard lithium aluminum hydride solution is used to calibrate the instrument both before and after the sample is run. A third setting allows the flame jet and sample line to be flushed with the solvent, tetrahydrofuran.

(C) The molarity of the excess lithium aluminum hydride can be established by reference to another graph (Figure 5) obtained from the same data as Figure 3. In this case the spectrophotometer reading resulting from an aluminum hydride solution containing a slight excess of LiAlH_4 is plotted against the molarity of the excess LiAlH_4 . It has been observed that the slope of this line is greater than that of LiAlH_4 by itself in tetrahydrofuran. The reason for this is believed to be a slight enhancement of lithium chloride solubility resulting from excess lithium aluminum hydride.

(2) The Flame Emission Spectrum of an Aluminum Hydride Solution (U)

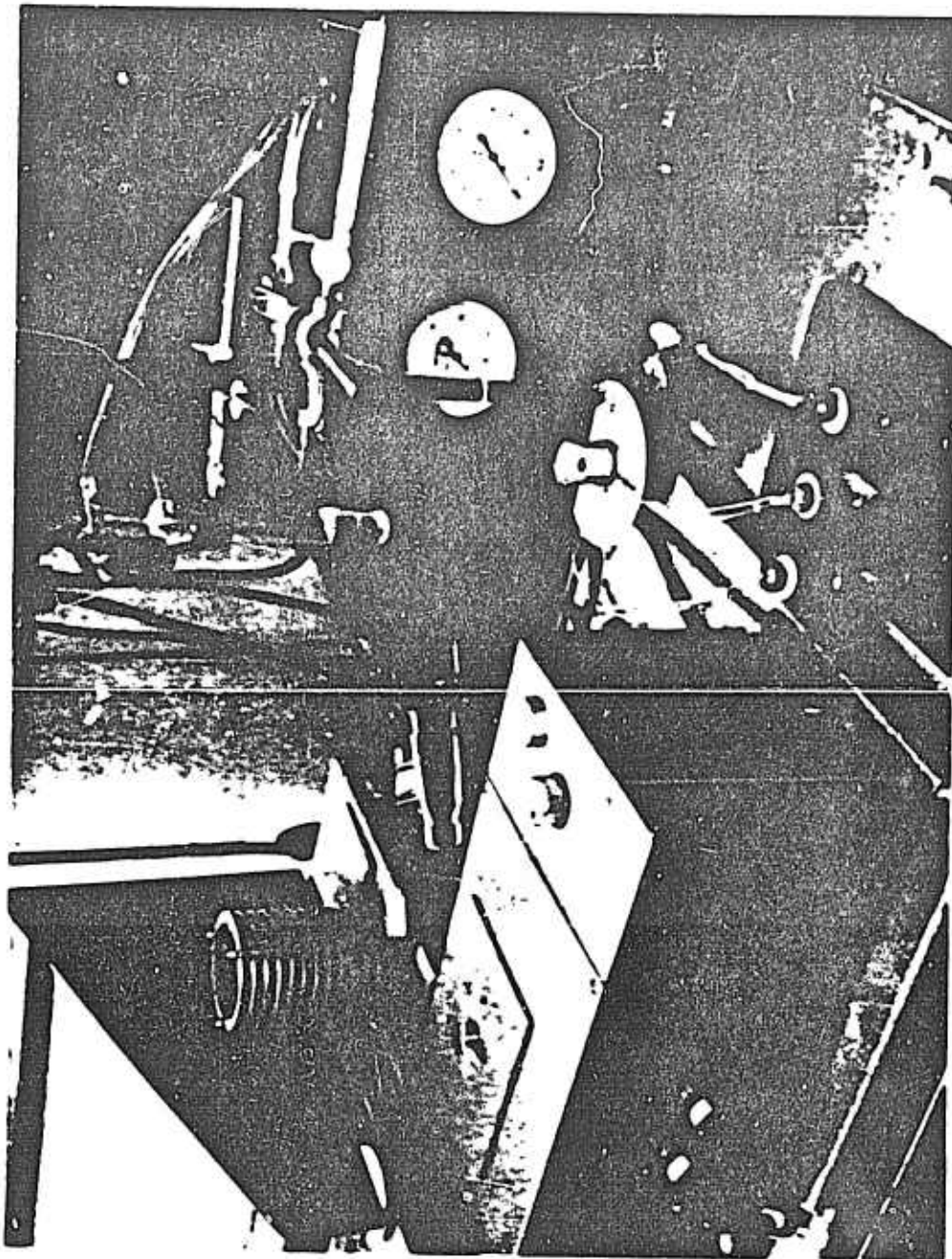
(C) In addition to determining lithium by flame photometry, it may also be possible to determine other elements such as magnesium, sodium and boron. In order to determine if any of these elements could be detected in an aluminum hydride solution containing a slight excess of lithium aluminum hydride, a flame spectrum was obtained between 3000 \AA and 9000 \AA as shown in Figure 6. Although no boron was present, it would be expected to have approximately the same sensitivity as aluminum.

(U) The elements which can be identified are sodium (5890 \AA) and lithium (6708 \AA); the remaining emission is due to carbon in the tetrahydrofuran. It should be noted that there is no interference from the solvent for lithium, while the sodium emission appears on a small shoulder. Sodium is present as an impurity even in the distilled tetrahydrofuran and therefore it may be difficult to determine very small amounts associated with the reaction. If larger concentrations appear as the result of a slightly soluble sodium salt, they should be reasonably easy to determine.

(U) Any emission due to aluminum is completely masked by the solvent, and the same result is expected for boron and magnesium. If flame analysis is to be used to determine these elements in the crystallizer solution, it will be necessary to hydrolyze the samples and obtain the emission of an aqueous solution.

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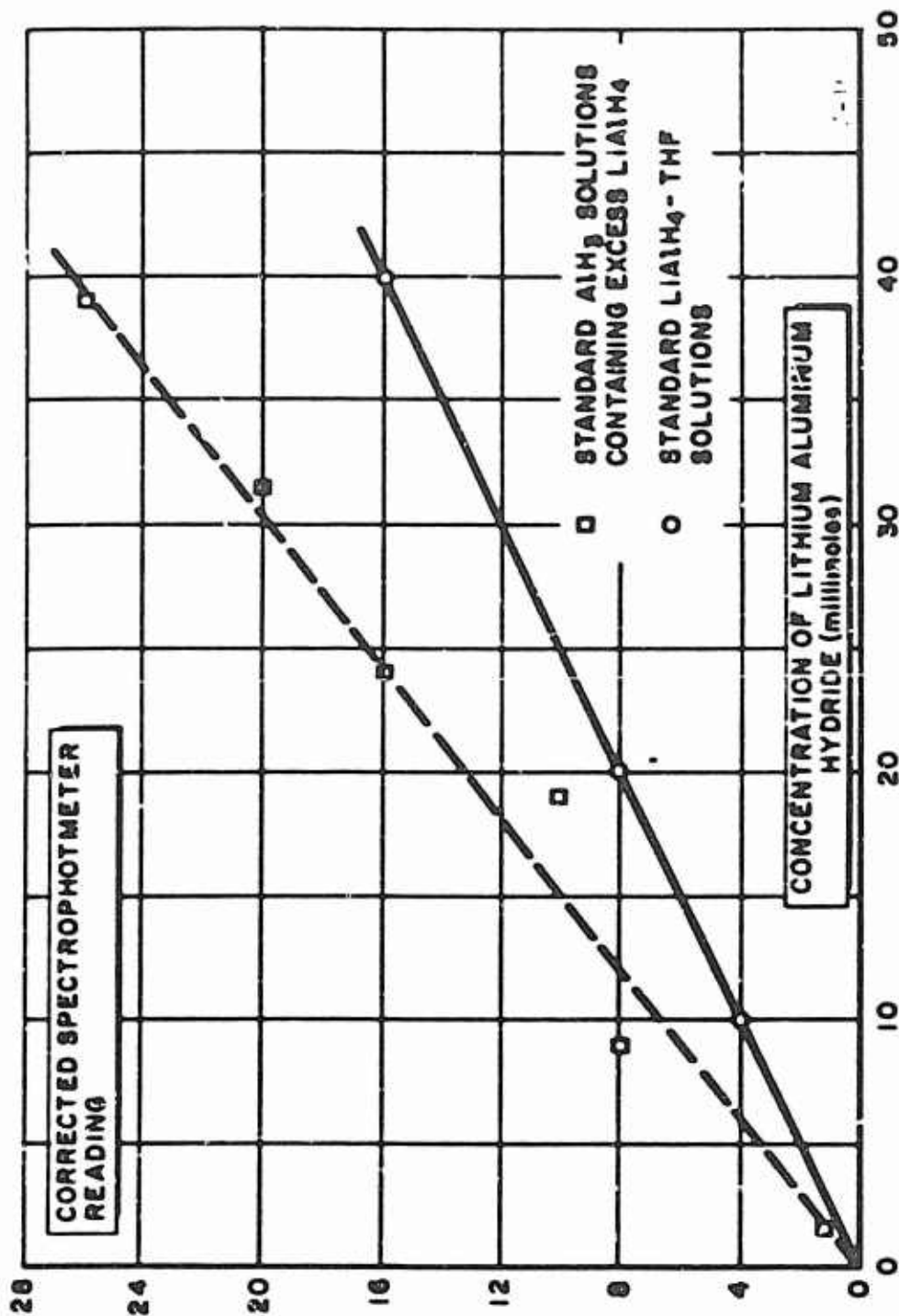
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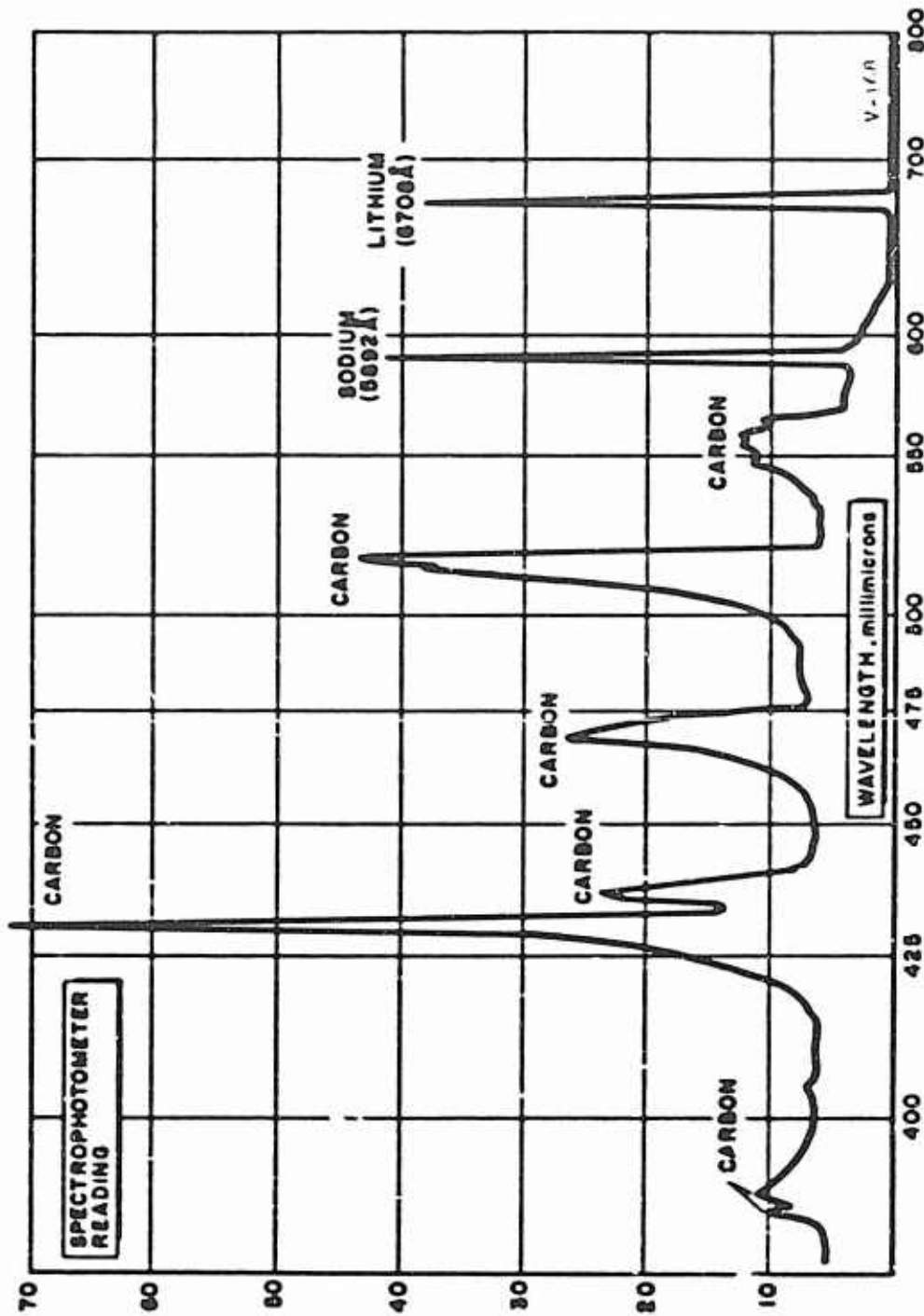
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(U) FIG. 5 - Plot of Absorbance as a Function of Lithium Aluminum Hydride Concentration

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(11) Fig. 6 - Flame Spectrum of an Aluminum Hydride Solution between 480 Å and 9000 Å

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1. Accurate Determination of Small Amounts of Water in Organic Solvents (U)

(C) In aluminum hydride crystallization it is important that the water content of the solvents be reduced to a minimum. A modified Gilbarco Sorption Hygrometer has been used for the past two years to determine small amounts of water in benzene and ether. While useful for this purpose, the instrument has the disadvantage of requiring quite long periods of time to reach stable operating conditions; in addition, it is necessary to wait 15-20 minutes between samples.

(U) A more rapid and accurate method of determining water is gas-liquid chromatography using the newly-developed porous polymer columns (2). This technique is now being used to determine water in organic solvents. Figure 7 shows a typical peak for water in benzene which has been dried with lithium aluminum hydride. Standard curves have been prepared, and it is now possible to determine water in benzene and ether below 10 ppm.

2. Development of a Continuous Crystallizer (U)

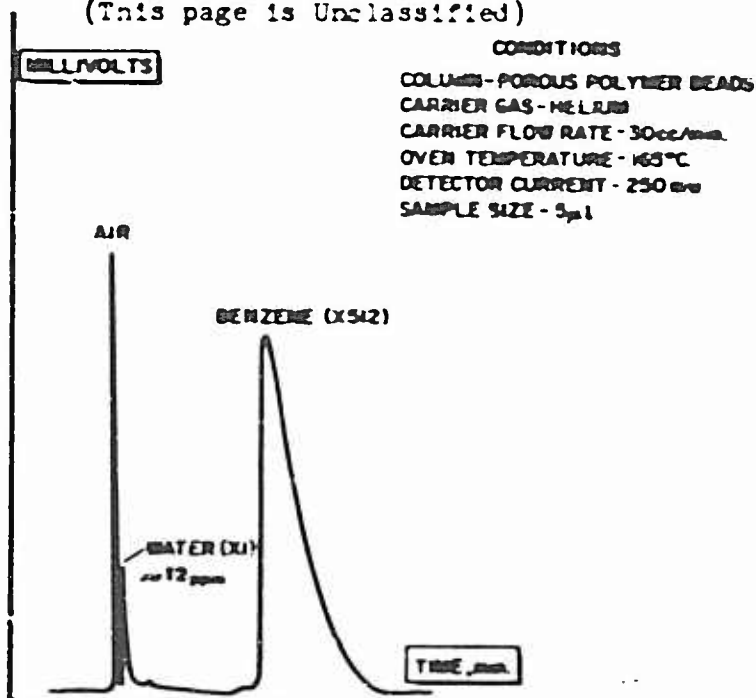
(C) The objective of the continuous crystallization work is the improvement of the properties of AlH_3-1451 , particularly the thermal stability. The goal is to develop a continuous crystallizer where precise control of the many parameters affecting the crystallization of aluminum hydride can be attained. Continuous crystallization of AlH_3-1451 was demonstrated in 1965 (1) with considerable progress made in the development of such a crystallizer. Specific objectives this year include:

- (i) Incorporation of magnesium into the crystal lattice and/or surface treatment of the crystalline product to improve thermal stability.
- (ii) Optimization of the crystallization parameters to improve the physical and chemical properties.
- (iii) Improvement of the continuous crystallization process.
- (iv) Supply of the "best" AlH_3-1451 that can be produced by current technology for characterization and evaluation.

(C) Considerable progress has been made in understanding and controlling the conditions required for reproducibly obtaining acceptable AlH_3-1451 nuclei. Significant advancements have also been made in the areas of solution stability, product adhesion and reaction stoichiometry. Finally, a technique has been developed to routinely incorporate magnesium into the crystal lattice of

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(U) Fig. 7 - Gas Chromatogram of Lithium Aluminum Hydride-Dried Benzene (Water Analysis)

AlH₃-1-51 made in the continuous crystallizer. These advancements, together with a discussion of results and parameter effects, are presented below.

a. Process Description (U)

(U) A modified draft-tube baffle (DTB) crystallizer was used to demonstrate the feasibility of continuous crystallization of AlH₃-1-51 in 1965 (1). Details of the operating principles of the DTB were also presented. Results obtained in this unit led to the design and installation of a Heresite-coated, tubular crystallizer in early 1966 and finally to a polyperfluorinated ethylene-propylene copolymer (Teflon FEP) lined unit of similar design. Details of the operating procedures and conditions are outlined below.

(1) Reaction (U)

(U) An ether solution of aluminum hydride is obtained by reacting ether solutions of AlCl₃ and LiAlH₄ in a batch reactor at ambient temperature. The ether has been previously distilled from LiAlH₄ and dried with molecular sieves. A slight excess of LiAlH₄ is used to assure complete reaction of the AlCl₃ and sodium borohydride is added to generate LiBH₄ in situ. Removal of the resulting insoluble chlorides by filtration and dilution with benzene

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in the crystallizer feed tank results in a 0.25-0.30 M aluminum hydride feed solution. Premature precipitation in the feed tank is not a problem at ambient temperature. Magnesium is introduced by adding an ether solution of $\text{LiMg}(\text{AlH}_4)_3$ to the feed tank.

(2) Crystallization (U)

(C) Schematic flow diagrams of the Heresite-coated tubular and the Teflon FEP-lined crystallizers are presented in Figures 8 and 9. Benzene, distilled from LiAlH_4 and dried with molecular sieves, is charged to the crystallizer and heated to 50°C . An ether solution containing AlH_3 , LiAlH_4 and LiBH_4 is then slowly fed to the boiling benzene to cause nucleation by the "thermal seeding" technique. After nucleation, a clear stoichiometric feed solution is prepared by the above procedure and added to the crystallizer. Analyses of a typical feed solution are presented in Table IV. The circulating magma temperature is then allowed to decrease to the desired operating temperature and controlled by the distillate removal.

Table IV

(U) Typical Aluminum Hydride Feed Solution Analysis

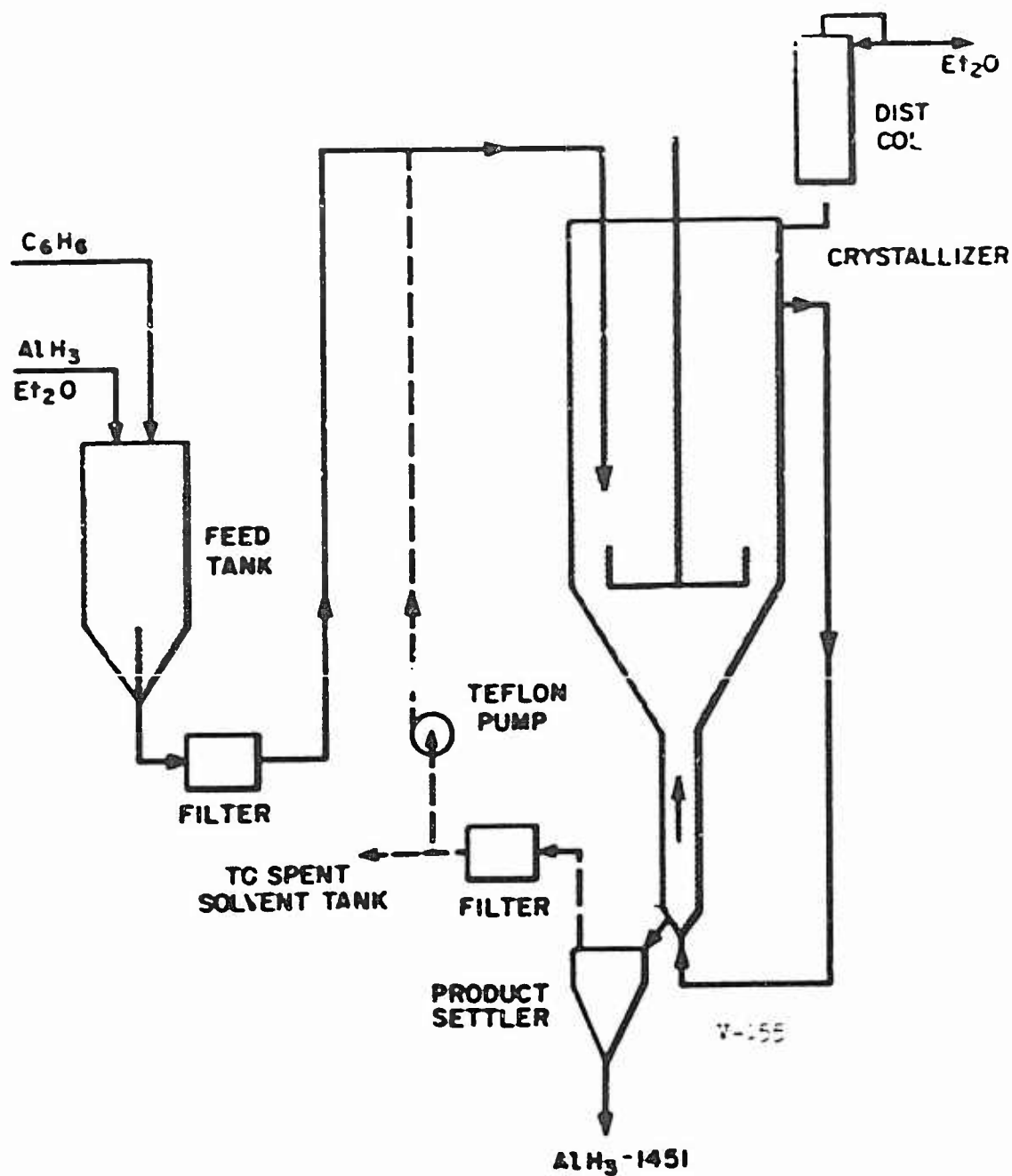
Compound	Concentration, M
AlH_3	0.2500
LiAlH_4	0.0100
LiBH_4	0.0008
LiCl	0.0005
NaBH_4	0.0004

(C) A product stream is continuously removed near the bottom of the elutriation leg and passed through a centrifugal separator where the AlH_3 -1451 crystals settle into a cold benzene reservoir. The supernatant liquor can be filtered to remove low density and/or high surface area particles and recycled by means of a Teflon diaphragm pump or removed from the system. If recycled, the stream is combined with the feed stream. The elutriation stream is removed near the surface and recycled to give internal classification of the crystalline product. A change in the operation of the polyperfluorinated ethylene-propylene copolymer (Teflon FEP) lined crystallizer was necessary to facilitate its operation. The reflux from the distillation column is used as the elutriation stream instead of removing mother liquor from the top of the crystallizer as in the Heresite unit. Several recent runs have been made without elutriation.

(3) Evaluation (U)

(U) Product samples are removed periodically, ether-washed by decantation, and vacuum dried. The recovered AlH_3 -1451

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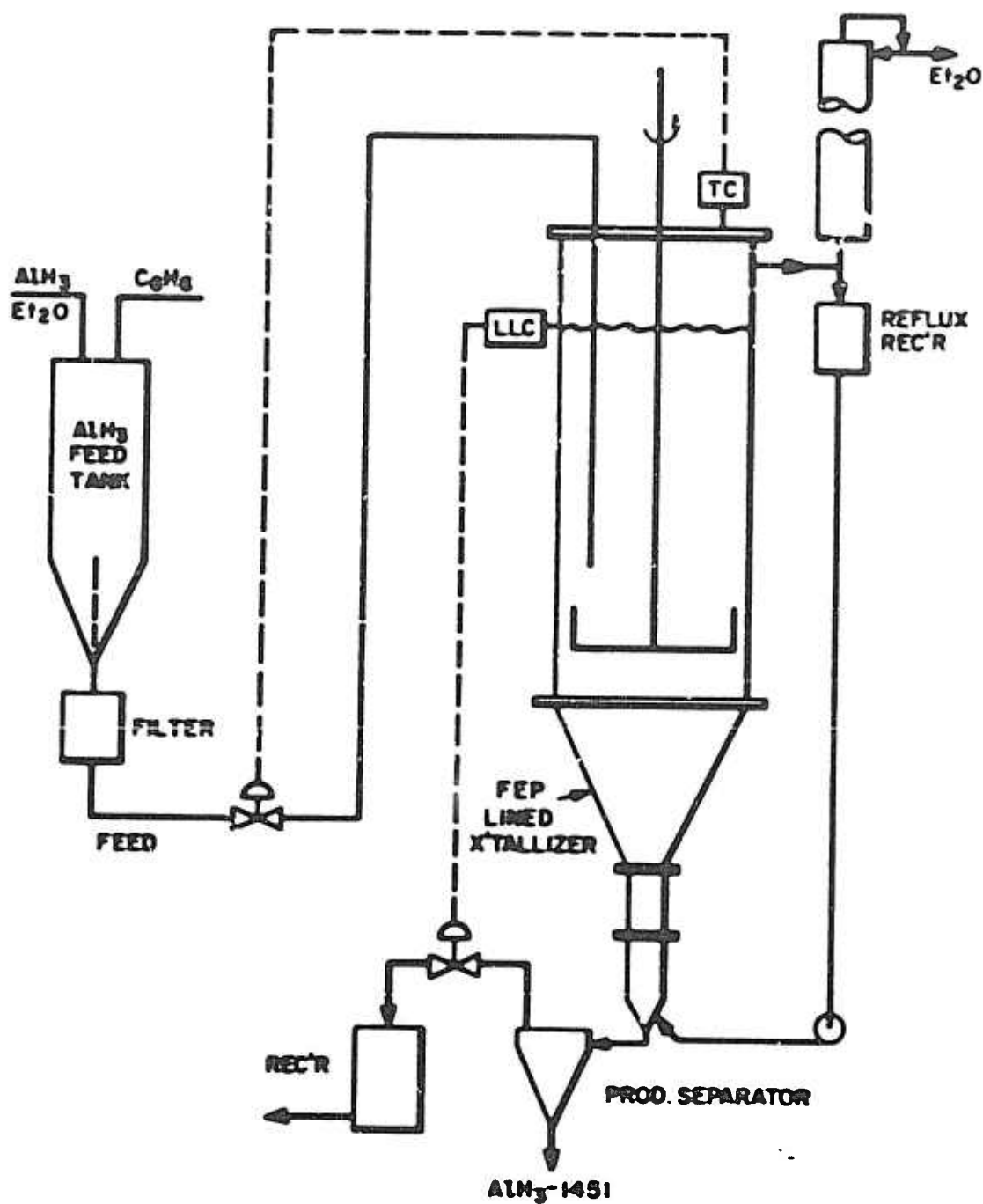


(C) Fig. 2 - Schematic Flow Diagram of Modified Aluminum Hydride Crystallizer

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(U) Fig. 9 - Teflon FEP-Lined Crystallizer

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is evaluated by a series of physical and chemical tests. These tests include microscopic examination of the particle configuration and crystallinity, X-ray diffraction analysis to establish hydride phase, bulk density, screen, and elemental analysis. Thermal stability is determined by the modified Taitani apparatus at 60°C

h. Results (U)

(C) One hundred forty-five runs, summarized in Table V, were made this year. Seventy-four of these produced AlH_3 -1451 with no contamination from other phases while others resulted in a mixture of AlH_3 -1-51, and AlH_3 -1444, AlH_3 1433, etc., or failed to nucleate properly. It should be remembered that this program was designed to study the crystallization process; therefore, 100% AlH_3 -1451 was not expected under all conditions. Most of the runs in the latter category can be explained either directly in the case of no nucleation or indirectly in the case of AlH_3 -1444 by the presence of impurities which inhibit nucleation until the upper concentration limit permissible for the formation of AlH_3 -1-51 is exceeded. A discussion of impurities and their effects is presented in a later section, A.2.c.(5).

Table V

(U) Summary of Aluminum Hydride Runs in the Continuous Crystallizer

Runs		Aluminum Hydride Phase Produced					
No.	h	1-51	1444	1433	1463	1435	A2
7	51	x					
13	16	x	x				
8	5.5	x	x	x			
9	4.0	x		x			
5	3.5	x			x		
3	2.0	x					x
1	3.0		x				
1	<1			x			
1	<1					x	
6	~0.0						Excessive Decomposition
14	9.5						Failed to Nucleate
145	100.0						

(C) All runs were continuous and varied in length from 3-17 hours, the shorter runs being those which failed to nucleate properly, where excessive decomposition occurred, or where the

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product adhesion rate exceeded the feed rate. Each of these areas is discussed in detail later. Product recovery continues to be low as product adhesion to the vessel wall remains a serious problem. A series of twenty-five runs in the Heresite-coated tubular crystallizer resulted in recoveries averaging 50%. However, these runs were less than four hours long as the rate of product adhesion on Heresite is a function of the run time. Some improvement in this area has been achieved with the Teflon FEP-lined crystallizer.

(2) Because of the difficulties with the Heresite-coated and Teflon FEP-lined units, the tubular crystallizer was recently coated with a new type of phenolic resin called "Phenolflex". This new coating is more flexible and hopefully more durable. Seven runs have been made in the unit with five producing 100% AlH_3 -1-51. Two of these runs have been operated for 17 hours, others of 12, 8, and 6 hours producing 135, 22-, 153, -5, and 33 g., respectively. One of the two runs not producing material was on the chloride side of stoichiometry and the other failed to nucleate properly, probably as a result of an attempt to restart the unit without the usual lengthy clean-up procedure. Yields from this unit have been in the range of 75-90%. The significant difference in the operation of the new unit is the much longer run time during which good product is produced.

(3) Although product adhesion is still a major problem in this new unit, it has allowed an important observation to be made. In the longer preparations, a build-up of an impurity, tentatively identified as lithium chloride by X-ray analysis, has shown some correlation with a decrease in the rate of product removal. This build-up of lithium chloride in the unit may be contributing to the product build-up on the walls and/or the slowing down of the rate of nucleation and crystal growth.

(4) Selected samples of product from runs which produced 100% AlH_3 -1-51 have shown improved physical and chemical properties. Single cubic-shaped crystals have been observed in several runs. These crystals are not "perfect" but are a definite improvement over crystals prepared by the batch technique. Bulk density and screen analysis have also been improved. Elemental analyses of untreated samples are comparable to the batch material. Thermal stability (1% decomposition at 60°C.) of untreated samples has ranged from 8-11 days with the best sample requiring nearly 19 days. The average magnesium-doped sample contains 0.9% to 1.0% and requires 10-14 days to decompose 1% at 60°C. Magnesium has been incorporated into concentrations up to 1.8%. The best sample contained 1.10% magnesium and required 28 days to reach the same level of decomposition. Recent samples have been surface treated with approximately 1% diphenylacetylene (DPA) with the preliminary data showing a 100% improvement in stability.

c. Continuous Crystallization Studies (U)

(1) Most of the work during this year has been concentrated on studying process parameters, improving solution stability,

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eliminating or reducing product adhesion and incorporating magnesium into the crystal lattice of AlH_3-1451 .

(1) Crystallizer Design (U)

(C) Three crystallizer designs have been evaluated, namely the Draft-Tube Baffle (DTB) crystallizer, the Heresite-coated tubular crystallizer, and the Teflon FEP-lined tubular crystallizer. All three units will produce 100% AlH_3-1451 with no significant differences in product quality, crystal adhesion to vessel walls or solution stability noted as a function of design. The operation of the tubular crystallizers is similar to the DTB.

(C) The design of the DTB crystallizer was discussed in detail in an early report (1). This crystallizer was relatively complex mechanically and made effective clean-up more difficult. The Heresite-coated, tubular unit eliminated the settling annulus and increased the L/D ratio to 3:1 and cone angle to 75° . A further increase in the L/D ratio to 6:1 was incorporated into the design of the Teflon FEP-lined unit.

(C) It is concluded from these evaluations that crystallizer design can and should be simplified as much as possible and that the L/D ratio should probably be between 3:1 and 6:1.

(2) Materials of Construction (U)

(C) The first two crystallizers were fabricated of Heresite-coated steel. Problems were encountered with scaling and pin holes in the coating, particularly around welds and at slope changes. Design modifications and conductivity checks of the coating prior to use improved the life of the coating but it did not eliminate completely the deterioration problem. Therefore, although Heresite is definitely compatible with the aluminum hydride system at operating conditions, it is doubtful that this material of construction is durable enough for commercial application in this process.

(C) An evaluation of other materials of construction was deemed necessary to eliminate product adhesion to the vessel walls. A fluorinated ethylene-propylene copolymer (Teflon FEP) resin was found to give outstanding results in the laboratory as discussed in Section A.1., including the essential elimination of product adhesion, a significant reduction in decomposition, increased yields, and a reduced clean-up time. As a result of this work, a tubular crystallizer was fabricated from stock items of Teflon FEP-lined pipe and fittings.

(C) Evaluation of the FEP-lined crystallizer is incomplete. Inspection of the vessel after four runs revealed that the lining in the 8" x 2" concentric reducer had sheared in the 2" nozzle due

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to stresses generated during fabrication. This break in the lining exposed the base metal, mild steel, to the crystallizer solution and resulted in excessive decomposition of the aluminum hydride. After several additional runs, the Teflon FEP-lining in the cone and on the bottom third of the cylindrical section deteriorated during a single run. X-Ray analysis of a sample scraped from the liner revealed AlP_3 (10-20%), and equal amounts of graphite and Teflon. This deterioration is apparently a reaction of either aluminum hydride and/or aluminum with the Teflon FEP. The nature of this reaction and the conditions required to initiate it are unknown. Run conditions and clean-up procedures were both normal. The only observed effect of the deteriorated surface is increased product adhesion. In addition to the above mechanical problems, a fire resulting from a $LiAlH_4$ -solution leak has also hampered the evaluation program.

(C) Heat transfer is a problem in the operation of the Teflon FEP-lined crystallizer. The calculated overall heat transfer coefficient is less than 10 BTU/hr/ft²/°F as compared to 50-75 for Pfaudler glass-lined vessels operated under similar conditions. The low heat transfer rate results because the Teflon FEP lining is not bonded to the base metal. A benzene vapor injection system which increases the total heat input has been operated, but effects of vapor injection on nucleation, crystal growth, etc., are unknown.

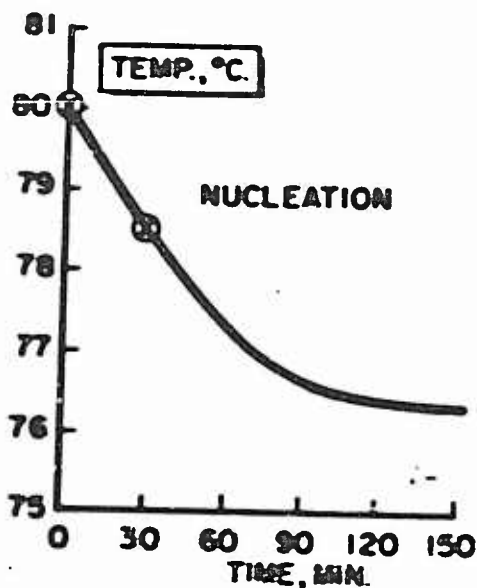
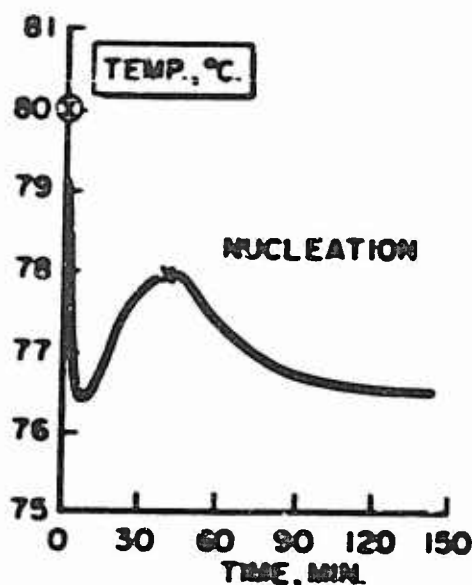
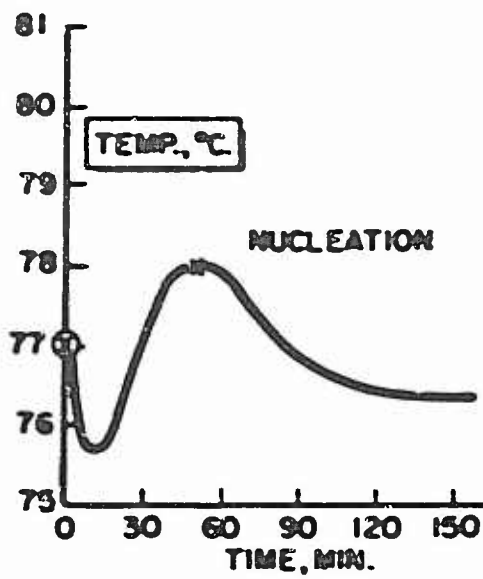
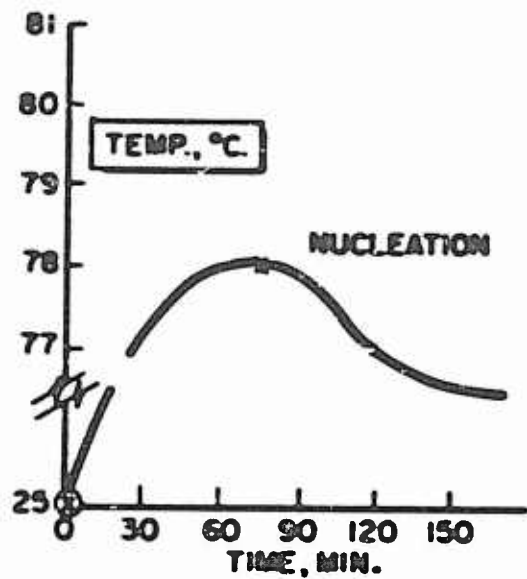
(C) In summary, the use of Teflon FEP is a significant step in the right direction. Product adhesion, although still present, is not of the same order of magnitude and may be related to operating parameters and/or crystallizer design. Similarly, heat transfer is a problem but it can be overcome by using other methods of heat input such as vapor injection, external heat exchangers, internal heat exchangers, etc. Additional work is required to fully evaluate the use of Teflon FEP.

(3) Nucleation (U)

(C) The mechanism and conditions of initial nucleation are extremely critical in determining the appearance and quality of the final AlH_3 -1451. Nucleation in the aluminum hydride crystallizer is accomplished by a "thermal seeding" technique. Four methods, as shown in Figure 10, have been evaluated with the most reproducible results obtained using Method 1.

(C) The first method consisted of adding an ether solution of aluminum hydride, lithium aluminum hydride, and lithium borohydride to ambient temperature benzene and heating until nucleation occurred. The long heating time resulted in excessive decomposition in the solution. The second method was adapted to reduce this heat treatment time. In this method the hydride solution was added to preheated benzene. The third method consisted of charging batch-wise the same solution to boiling benzene. This method resulted in a temperature drop without nucleation occurring. By reheating the solution to a higher temperature,

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② NUCLEATION FEED SOLUTION ADDED TO CRYSTALLIZER

(U) Fig. 10 - "Thermal Seeding Nucleation Methods (Time - Temperature Profiles)"

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nucleation could be obtained. The fourth method is a variation of the third with the initial feed introduced over a period of time (20-30 minutes), maintaining a high temperature, thus a low ether concentration.

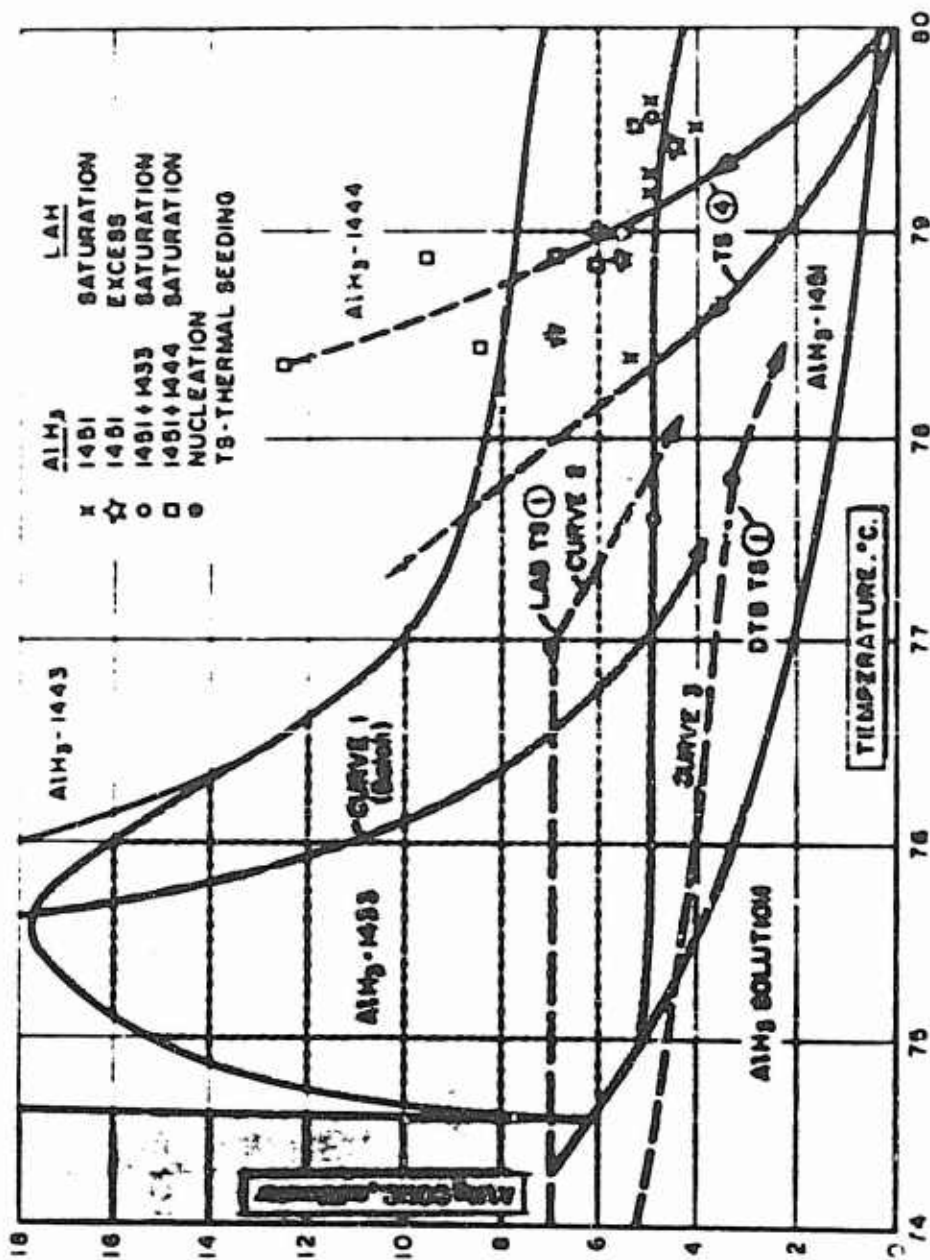
(C) The apparent nucleation mechanism, if the conditions are right, is directly to well-formed cubes of $\text{AlH}_3\text{-1-51}$. The degree of crystallinity tends to degenerate with time since the crystal growth rate is rapid; some agglomeration has also been noted. Finally, it is essential to eliminate concentration gradients in the crystallizer to prevent the continuous nucleation of the undesirable $\text{AlH}_3\text{-1-44}$ phase.

(C) Further consideration of nucleation data generated in the continuous crystallizer shows that the controlling parameters are the aluminum hydride concentration, the temperature (ether concentration), and the additive hydride concentration. Since aluminum hydride exists in at least seven polymorphic, non-solvated crystalline forms and several solvated crystalline forms, it is impractical to develop a true phase diagram showing the relationship of the various aluminum hydride crystalline phases, aluminum hydride concentration, temperature, ether concentration, additive hydride concentration, etc. However, a working diagram which fits existing data has been developed and is presented in Figure 11. The aluminum hydride concentration is based on the total volume of solvent present in the crystallizer at the time of nucleation. The temperature is a function of the ether concentration as it represents the boiling point of the ether - benzene solvent system at atmospheric pressure.

(C) Nucleation in the "batch" crystallizer is shown by Curve 1 in Figures 11 and 12; because of the expanded scale only the lower part of the curve is used for Figure 11. In this case the molar concentration at nucleation is approximately 0.09 M at 75.2°C . with nucleation occurring as $\text{AlH}_3\text{-1-43}$ and proceeding through $\text{AlH}_3\text{-1-43}$ to $\text{AlH}_3\text{-1-51}$. $\text{AlH}_3\text{-1-44}$ was obtained if the temperature was too low or too high at nucleation. Curve 1 is typical of a large number of runs made under these conditions.

(C) In the continuous crystallization studies in the laboratory using the "thermal seeding" technique (Method 1), the concentration of aluminum hydride was initially set at 0.0067 M. Nucleation in this case occurred as $\text{AlH}_3\text{-1-43}$, followed by conversion to $\text{AlH}_3\text{-1-51}$. This method is represented by Curve 2 in Figure 11. The same technique and concentration, however, resulted in direct nucleation of $\text{AlH}_3\text{-1-51}$ in the DTB crystallizer. It is believed that the difference resulted from a significant amount of decomposition in the DTB unit at the time of these studies which reduced the concentration at nucleation to 0.004-0.005 M, as shown in Curve 3, Figure 11. Nucleation at concentrations lower than 0.005 M in the laboratory does result in the direct nucleation of $\text{AlH}_3\text{-1-51}$ as would be expected. Again, Curves 2

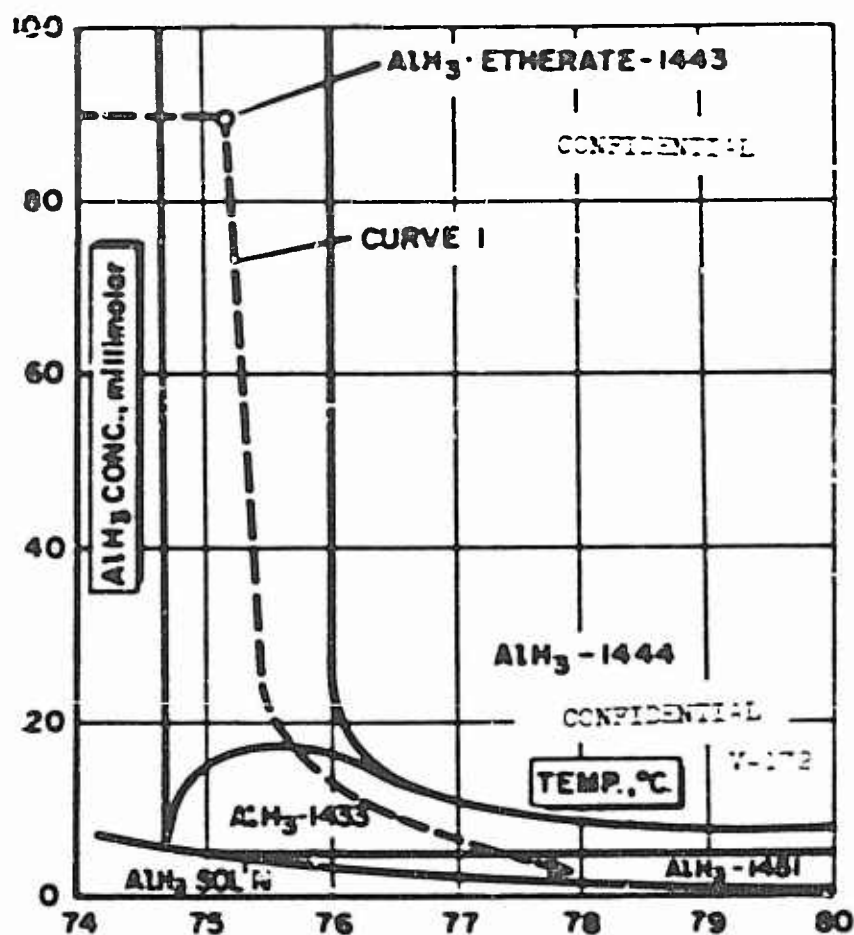
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(U) Fig. 11 - Expanded Working Phase Diagram for Aluminum Hydride in the Diethyl Ether - Benzene System

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(U) Fig. 12 - Working "Phase Diagram"
for Aluminum Hydride in the Diethyl Ether - Benzene System

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and 3 are typical of a large number of runs made under these conditions. Results obtained using the "thermal seeding" techniques in Methods 2 and 3 can be similarly interpreted. Data for several runs using Method 4 are also shown in Figure 11. Additional runs using Method 4 have substantiated the conditions required for direct nucleation of $\text{AlH}_3\text{-1451}$.

(C) The fundamental difference between Method 4 and the other three "thermal seeding" techniques and the "batch" technique should be noted by reference to Figure 11. Instead of approaching the nucleation temperature from the left (AlH_3 in solution), nucleation by Method 4 proceeds from the right according to the solid line (TS4). If nucleation proceeds in a normal manner, the aluminum hydride concentration remains below 0.005 M with approximately the same amount being removed by crystal growth as is added by solution. If for some reason (impurities, etc.) nucleation does not occur, the aluminum hydride concentration increases above 0.005 M (broken line) and enters a region where $\text{AlH}_3\text{-1444}$, $\text{AlH}_3\text{-1-33}$ and other extraneous phases nucleate.

(C) It is apparent from these data that the aluminum hydride concentration at nucleation is a controlling factor. The upper concentration limit to obtain $\text{AlH}_3\text{-1451}$ directly is approximately 0.005 M. Concentrations above this limit usually yield $\text{AlH}_3\text{-1444}$ at the higher temperatures. The one exception is when a large excess of lithium aluminum hydride is present in the crystallizer at nucleation. This tends to expand the region for direct nucleation of $\text{AlH}_3\text{-1451}$ (starred results) and appears to play a role in the nucleation mechanism. Finally, it should be emphasized that the exact shapes of the phase curves, their exact location on the diagram, and the relative areas are only approximate and represent a valuable working diagram consistent with all available data.

(4) Parameter Studies (U)

(C) The most significant parameters in the aluminum hydride crystallization process are believed to be agitation, crystal retention time, feed rate and additive hydride concentration. These and other parameters studied are discussed below.

(a) Agitation (U)

(C) Agitation affects the crystallinity of $\text{AlH}_3\text{-1451}$ and the crystal retention time, but has little, if any, effect on product adhesion to vessel walls. The effect on product agglomeration is not known. These conclusions are based on observations made in a large number of runs in which three types of agitator designs were evaluated. Designs include propeller, anchor, and turbine types operated with and without draft tubes, and with both upward and downward draft. Speed has been varied from 50-300 rpm. The use of baffling has not been thoroughly examined, as internal surface area has been minimized due to the product adhesion problem.

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(see Section A.2.c.(7)). No significant crystal breakage was observed under any of the experimental conditions outlined.

(U) The degree of crystallinity improves as the severity of agitation decreases. This effect is normally less pronounced than the effect of LiAlH_4 on crystal growth and/or the crystal retention time in the crystallizer. Agglomeration is also a function of LiAlH_4 concentration and crystal retention time, with the latter a function of agitation. The centrifugal effect of some agitator designs, e.g., the anchor agitator, tend to swirl the solution, forcing the more dense crystals to migrate to the wall. At the higher speeds, the centrifugal force is larger than the gravitational force and results in excessive crystal retention times. This can be eliminated by the use of baffling and/or by recycling a stream through a product separator. Product adhesion to vessel walls was not significantly altered by any of the agitation systems evaluated.

(U) Until the product adhesion problem is solved, a shrouded turbine, which produces primarily axial flow patterns, is recommended. The shroud should be part of the agitator to minimize internal surface area and maintain a smooth wall. Once the adhesion problem is solved, agitation should be further studied to select, optimize, and establish design criteria for scale-up.

(b) Crystal Retention Time (U)

(U) An approximate crystal retention time was established for the DFB crystallizer for runs without a continuous recycle product stream. It was found that the average time was 1.5 hours which is long for the heat-sensitive aluminum hydride. It was concluded that the average retention time of crystals should be considerably reduced. This was accomplished by installing an all-Teflon pump to continuously recycle the product stream through a product settler. A similar technique was used on the heretofore-coated tubular unit. To further reduce the crystal retention time, the elutriation stream was not used in the Teflon PEP unit; however, no control of the particle size range was possible. It is obvious that the retention time should be minimized, but as with agitation, it cannot be accurately controlled until product adhesion is solved.

(c) Feed Rate (U)

(U) A range of feed rates varying between 0.003 and 0.032 moles of aluminum hydride per liter of crystallizer per hour was studied early in the year. It was apparent from the results that the feed rate affects both the nucleation and growth mechanisms. Some runs nucleated as AlH_3 -1-51, but, due to limited surface area for growth, renucleated some time later as AlH_3 -1-33 and/or AlH_3 -1-44. Later in the year runs were made with a feed rate of approximately 2 moles of aluminum hydride per hour (0.06 mole/liter/hour)

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demonstrating that $\text{AlH}_3\text{-}1451$ can be crystallized at significantly higher feed rates. The maximum rate depends on many factor such as nuclei size, distribution, effects of impurities, etc., and has not been established. Rates up to 0.13 moles/liter/hour have been used in laboratory back-up work.

(d) Feed Concentration (U)

(C) Solubility data of the etherate of aluminum hydride in diethyl ether have been presented previously (3). A method was developed to permit the holding of more concentrated solutions. Recently 1 M ether solutions of aluminum hydride have been successfully used. These solutions were made by reacting ether solutions of AlCl_3 , and LiAlH_4 at 0°C . and maintaining the resulting solution at that temperature. More concentrated solutions were used in the laboratory to make $\text{AlH}_3\text{-}1451$ and should, therefore, prove practical on a larger scale.

(C) The more concentrated feed solution permits the addition of more aluminum hydride per unit volume of ether, which must be removed as distillate. Another method of accomplishing the same objective is by diluting the feed solution with benzene, maintaining the concentration, based on total volume, constant. This has also been evaluated using benzene concentrations in the feed solution up to 75 volume % with an aluminum hydride concentration of 0.25 M, i.e., a concentration of 0.75 M based on ether alone. Higher benzene concentrations are possible; however, premature precipitation of the aluminum hydride sometimes occurs. The disadvantage of this technique is the increased amount of solvent recycle required.

(e) Feed Injection Point (U)

(C) The position of the feed injection point was found to be critical for proper nucleation of $\text{AlH}_3\text{-}1451$. If it was placed in a position where concentration gradients could exist, a mixture of $\text{AlH}_3\text{-}1451$ and $\text{AlH}_3\text{-}1444$ phases resulted. Proper nucleation of $\text{AlH}_3\text{-}1451$ without other phases was obtained by injecting the solution through a dip pipe into the bulk of the circulating magma near the agitator.

(f) Additive Hydrides (U)

(C) The early runs in the DTB crystallizer contained both LiAlH_4 and LiBH_4 in equal concentrations. Problems were encountered in keeping both hydrides in solution in the continuous process, and it became necessary to study the effects of each of these additives. It was known that $\text{AlH}_3\text{-}1451$ could not be made unless LiAlH_4 was present, but the necessity of LiBH_4 was in doubt. Work was therefore initiated to evaluate the effect of LiBH_4 . Originally, NaBH_4 was added to the reactor to generate some LiBH_4 in situ. In later runs the only LiBH_4 present was that generated during the NaBH_4

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treatment step. It was found that LiBH_4 was not required to nucleate and grow AlH_3 -1451. Furthermore, product quality did not appear to be affected, as product from a series of runs was white AlH_3 -1451 possessing a cubic crystal habit and a thermal stability of 7 to 10 days before reaching 1% decomposition at 60°C . Other physical and chemical properties were comparable to material made with LiBH_4 present. Later work has shown, however, that LiBH_4 in the initial feed solution gives more consistent nucleation, especially when the hydride has been doped with magnesium. It is concluded from this work that LiBH_4 is not needed in the continuous process where "steady state" conditions can be attained, but does have a beneficial effect on nucleation. This is probably related to the increased solubility of LiAlH_4 .

(C) Excess LiAlH_4 also creates problems during crystallization since it becomes extremely difficult to maintain the optimum concentration. The feed solution must contain a very slight excess of LiAlH_4 which is necessary for desolvation yet the increase in concentration must be held to a minimum during crystallization. During the first part of the year stoichiometry problems prevented direct control of the LiAlH_4 concentration, but after the flame photometry technique was developed the exact amount of LiAlH_4 in the feed solution could be determined. This analysis resulted in much better control of this parameter.

(C) Magnesium is incorporated into the crystal lattice of AlH_3 -1451 by adding an ether-soluble magnesium specie, $\text{LiMg}(\text{AlH}_4)_3$, to the aluminum hydride feed solution. The incorporation of magnesium is discussed in a later section.

(g) Temperature (U)

(C) The temperature of the crystallizing medium is a direct function of the ether concentration in the ether-benzene solvent since all work has been done at atmospheric pressure. The effect of equilibrium temperature ranging from 75°C - 78°C . (8 to 4 wt. % ether) has been evaluated with essentially no effect on growth observed. The equilibrium solubility of aluminum hydride is too low for growth above 78°C . and too high for nucleation as AlH_3 -1451 below 75°C . The temperature for nucleation, however, is critical.

(5) Types of Decomposition (U)

(U) The decomposition of aluminum hydride on the vessel walls has been a major problem in the development of the continuous crystallizer. Three types of decomposition during crystallization have been defined. One is related to the thermal sensitivity of the material and the other two are related to the presence of impurities. Techniques have been developed to effectively control the rate of decomposition in the crystallizer for periods up to 8-10 hours.

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(a) Thermal (U)

(C) One type of aluminum hydride decomposition is thermal. It is a function of the time the aluminum hydride is in the crystallizer at the elevated temperatures required for desolvation and crystallization. This type of decomposition can be controlled by:

- (i) Decreasing the crystal retention time.
- (ii) Reducing the crystallizer wall temperature.
- (iii) Reducing the crystallizer solution temperature.

The first two approaches have been actively pursued and have resulted in an improved product. It appears, however, that the minimum temperature for crystallization is about 75°C.; below this the rate of desolvation and conversion becomes too slow for practical use. The optimum temperature appears to be between 75°-80°C., which is the range of the ether - benzene system being used.

(b) Catalytic Surface Decomposition (U)

(U) Another type of decomposition is catalytic surface decomposition, caused by impurities on the surface of the vessel wall. This type can be controlled by using a non-porous material of construction such as polyperfluoroethylenepropylene copolymer (Teflon FEP) and/or by surface treating the crystallizer just prior to start-up with a very dilute ether-benzene solution of lithium aluminum hydride. The latter technique has been demonstrated on both glass and Heresite in the laboratory and in the larger scale crystallizer.

(c) Solution Decomposition (U)

(C) Solution decomposition is caused by impurities in the crystallizing solution; it is also related to the compatibility of the materials of construction with the aluminum hydride at process conditions. The only effective way to control this type of decomposition is by quality control techniques and the selection of compatible materials of construction. Quality control is a significant part of the existing program.

(U) Impurities are introduced from various sources including raw materials (AlCl_3 , LiAlH_4 , diethyl ether, benzene), reaction by-products (LiCl , AlH_2Cl , etc.), the atmosphere (O_2 and H_2O), cleaning residues (HCl , H_2O , and/or reaction products) and aluminum from the decomposition of aluminum hydride.

(U) Impurities in the aluminum chloride are primarily trace metal chlorides. A typical emission spectroscopic analysis is shown in Table VI. The preparation procedure of aluminum chloride solution includes a hydride treatment step with either

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NaBH_4 , NaAlH_4 , or LiAlH_4 . It is believed that this treatment removes the transition metals (Fe, Zn, Ti, etc.) which are known to be detrimental to the stability of aluminum hydride. Emission spectroscopic analysis of the aluminum chloride solid after treatment does not reveal a noticeable difference in concentration of any of the detectable metal ion(s), but the presence of Ti and Zn in the hydride residue has been identified by X-ray analysis.

Table VI

(U) Typical Emission Spectroscopic Analysis
of Reagent Grade Aluminum Chloride

<u>Metal</u>	<u>Concentration, ppm</u>
B	<25
Ca	<250
Cd	<50
Co	<50
Cu	<25
Cr	<25
Fe	190
Mg	<39
Mn	<5
Ni	<25
Pb	48
Si	70
Sn	<50
Ti	<25
V	<50
Zn	<100
Zr	<50

(U) The lithium aluminum hydride is approximately 95% pure as determined by elemental analysis. The insoluble portion, which is removed by filtration, contains oxygen as determined by neutron activation analysis. It is believed that the resulting lithium aluminum hydride solution is free of detrimental impurities with the possible exception of trace amounts of LiCl .

(U) Mallinckrodt diethyl ether, Grade 0848, appears to be free of detrimental impurities. The benzene is monitored for impurities, including sulfur (<5 ppm), unsaturation, and aromatic and aliphatic compounds. All of the ether and benzene is distilled

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from lithium aluminum hydride and treated with molecular sieves prior to use. Impurity build-up in the recycle benzene is suspected; however, efforts to isolate and identify any species have failed.

(C) It is known that soluble chlorides such as $AlCl_3$, $LiCl$, AlH_2Cl , etc. will inhibit nucleation and/or initiate decomposition. The effects are noted when the feed concentration of soluble chlorides exceeds 0.001 M (a mole ratio of 1 Cl:300 AlH_3). Soluble chlorides are removed by reaction with $NaBH_4$ in a feed treatment step.

(C) Contamination from air (O_2 and H_2O) is known to affect nucleation and stability as well as cause phase problems (AlH_3 -1717 and AlH_3 -1563). The clean-up procedure includes the purging of all equipment prior to use with copious amounts of nitrogen supplied from a liquid nitrogen source. Water and oxygen analyzers are used to monitor the concentrations of these impurities in the ppm range. Cleaning residues which can remain in the crystallizer include HCl , H_2O , etc. The cleaning procedure includes several steps to minimize residues.

(C) The catalytic decomposition of aluminum hydride on the vessel walls is primarily a surface phenomenon and may be related to diffusion of impurities to and/or into the surface of the vessel wall. A treatment of the vessel with lithium aluminum hydride has significantly reduced the amount of this type of decomposition.

(C) Careful observations of the crystallization system have shown a residue always forms in the distillation column, condenser, and solvent recovery still. In addition, a flocculent solid was recently recovered from the recycle benzene storage tank. Further searching revealed a solid coating on the packing in the solvent recovery column. Elemental analysis of a sample recovered from the column showed the following weight percent: C, 6.5, H, 2.2; Al, 25.7; B, 2.6; Li, 4.2; O, 57.0, giving a material balance of 98.2%. This material is known to be detrimental to both the nucleation and thermal stability of AlH_3 -1451. However, it is not known how this material is formed or how it is carried to the top of the distillation column and to the solvent tanks.

(6) Cleaning Procedure (U)

(C) The cleaning procedure for the crystallizer is extremely critical in controlling aluminum hydride decomposition during processing. The procedure is time consuming and detailed. It consists essentially of the following steps:

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- (i) Acidizing with a 5-6 wt. % solution of hydrochloric acid at elevated temperatures.
- (ii) Rinsing thoroughly with distilled water (condensate).
- (iii) Air drying at elevated temperatures for 2-3 hours.
- (iv) Purging with gaseous nitrogen to remove air.
- (v) Benzene distillation to azeotrope the remaining water.
- (vi) Treatment of the crystallizer surface with a dilute ether-benzene solution of lithium aluminum hydride.

(U) The above procedure has been evolved over the past 18 months and is now the standard operating procedure. Various other steps such as HF treatment, ether rinses, acetone rinses, etc. have been evaluated and rejected. Attempts are continually being made to further improve solution stability by improving the clean-up procedure. Techniques to reduce the time required for clean-up were investigated, but additional work is required in this area.

(C) Treatment of the aluminum hydride crystallizer with a dilute solution of lithium aluminum hydride in an ether - benzene solvent system has been demonstrated to effectively control aluminum hydride decomposition on vessel walls. The procedure includes the addition of a small amount of lithium aluminum hydride solution to the crystallizer containing a mixture of ether and benzene. The solution is then heated, while being agitated, and drained to the spent solvent tank. The treatment is effective in benzene, but solids (LiAlH_4 and/or reaction products) precipitate and are difficult to remove. The concentration of lithium aluminum hydride in the crystallizer based on the total volume of solvent present has been varied from 0.7-2.5 mmolar. The treatment is beneficial at the low concentration but is not as effective below about 1.0 mmolar. The treatment time has been varied from one-half to two hours and the temperature from ambient to 80°C . with little change in effectiveness. It is believed the LiAlH_4 is reacting with impurities in the pores of the vessel walls and/or with the Heresite surface, thereby passivating the surface. This treatment technique is being further evaluated with the FEP-lined vessel.

(7) Product Adhesion (U)

(C) Adhesion of AlH_3 -1451 to the vessel walls of the crystallizer remains a problem. It is not a function of crystallizer design or degree of agitation but is increased by the presence of

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solid lithium aluminum hydride. The adhesion rate to Pfandler glass and Heresite increases with run time with the "point of diminishing return" reached in 3-5 hours after nucleation. In a recent series of runs (25) in the Heresite tubular crystallizer, the run time was limited to 3-4 hours with product recovery averaging 50-60 wt. %. Runs under the same conditions, but longer, result in significantly lower recovery.

(C) Laboratory work, detailed in Section A.1., revealed that product adhesion could be essentially eliminated by using Teflon FEP. This work led to the installation of the nine-gallon FEP-lined crystallizer discussed earlier. Adhesion does occur in the larger scale unit; however, it is radically different from that obtained on either the Pfandler glass or Heresite surfaces. The adhesion occurs in the form of "sheets" of crystals, analyzed by X-ray diffraction as 100% AlH_3 -1451, which "flake" after a period of time. This indicates that the product is not tightly bound to the surface as is the case in both the Pfandler glass and Heresite units. A water spray will remove most of the coating at the end of a run whereas acidizing is required in the other units. Based on these observations and laboratory data presented in Section A.1., the adhesion may be a function of crystallizer design, agitation, inner wall temperature or some other system parameter.

(C) In summary, the use of Teflon FEP is a significant step in the right direction. Product adhesion, although still present, is not of the same order of magnitude and may be related to operating parameters and/or crystallizer design. In addition, other similar materials of construction should be evaluated. Additional time is required to evaluate these alternatives and to develop a crystallizer which can be operated for several hours at realistic feed rates with minimal product adhesion.

(8) Incorporation of Magnesium (U)

(C) Magnesium is routinely incorporated into the crystal lattice of AlH_3 -1451 via the continuous crystallizer using the solution technique developed in the laboratory. The doping agent has been shown to be the complex hydride, $\text{LiMg}(\text{AlH}_4)_3$. A maximum magnesium concentration of 1.83 wt. % has been incorporated. The magnesium yield averages nearly 100%, i.e., essentially all the magnesium added to the feed solution is incorporated into the AlH_3 -1451 lattice.

(C) The early runs were plagued with precipitation of the doping agent, $\text{LiMg}(\text{AlH}_4)_3$ during crystallization, particularly at nucleation where the ether concentration was low. This has been eliminated by increasing the concentration of the additive hydride, LiAlH_4 , and by adding LiBH_4 to the feed solution.

(C) The effect of the magnesium on product stability remains a question. Some samples show improvement; for example, run

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163 A (1.10% magnesium) required 28 days to reach 1% decomposition, while others, such as 176 A (1.18% magnesium), decompose more rapidly than the normal material. Similar abnormalities exist in the non-magnesium-doped samples. The average normal sample requires 8 to 10 days to reach the 1% decomposition level, whereas 154 A required 19 days to reach the same level of decomposition.

(9) Reaction Stoichiometry (U)

(U) A technique has been developed to determine the exact stoichiometry of the aluminum chloride-lithium aluminum hydride reaction using a flame photometric method. Details of the experimental work and the procedure are presented in Section A.1.1. This method has been made standard operating procedure for the continuous crystallizer runs.

(10) Post Treatment (U)

(C) Selected samples have been treated with an ether solution of diphenylacetylene (DPA) using techniques developed in the laboratory and discussed in Section A.1. Results are too preliminary to draw any conclusions; however, based on laboratory data, treatment of the hydride before vacuum drying significantly improves product stability.

(11) Production (U)

(C) A goal of this work was to produce samples of the best possible quality AlH_3 -1451 for complete characterization. Difficulties with product adhesion have slowed production, but pound samples have been supplied to selected organizations.

B. FUNDAMENTAL DECOMPOSITION STUDIES OF ALUMINUM HYDRIDE-1451 (U)

(U) Efforts to develop a sound theoretical explanation for the decomposition of aluminum hydride have been made throughout the past year. Taliani data, X-ray data the theory of color development, and the principles of solid state physics have been applied to this problem in the belief that a better understanding of the processes will lead to improved methods of stabilizing AlH_3 -1451.

1. Mechanism of Decomposition (U)

(U) Previous studies suggest that the decomposition of aluminum hydride should be interpreted in terms of a three-stage process:

- (1) The initial reaction occurring at the surface of the crystals,



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- (ii) The formation of stable aluminum nuclei.
- (iii) The reaction occurring at the interface between the $\text{AlH}_3\text{-}^{145}\text{I}$ and the aluminum metal.

The last two processes, nucleation and nuclei growth, are independent and will vary with time, but the nucleation process is probably the more important if the thermal stabilization of aluminum hydride is considered.

(U) Data accumulated from various decomposition studies substantiate the belief that the initiation of decomposition occurs primarily at the surface of the hydride crystals. As a result, there is a particular interest in further understanding and elucidating the mechanism involved in the first stages of the decomposition process.

a. The Formation of Stable Aluminum Nuclei in the Lattice by Radiant Energy and Electrical Fields (U)

(U) The formation of stable aluminum nuclei primarily at the surface of the $\text{AlH}_3\text{-}^{145}\text{I}$ lattice is believed to be the result of a three-step process as follows:

- (i) The diffusion of a non-equilibrium concentration of anion vacancies through the hydride by a vacancy transfer method.
- (ii) The formation of "germ nuclei" by capture of electrons by the vacancies at the surface, imperfections, or grain boundaries.
- (iii) The coalescence of "germ nuclei" to form active growth nuclei.

(U) Closely associated with these phenomena are the appearance of color in aluminum hydride and its behavior as a semi-conductor (4). At elevated temperatures it usually changes to an off-white or gray after only a few tenths of a percent decomposition, gradually changing to black with increasing decomposition. Ultraviolet irradiation, visible light irradiation, electron bombardment, and gamma irradiation of the hydride change its color from white to light brown or black.

(U) The formation of color centers by irradiation is probably due to a displacement of the elements in the solid lattice from their equilibrium position; this gives rise to an electronic imbalance in the solid and results in an excited state for the solid with an accompanying loss of symmetry of the bonding electrons in the $\text{AlH}_3\text{-}^{145}\text{I}$ lattice.

(U) Color center formation is a function of the thermodynamic temperature and susceptibility of the solid to radiation (5). The

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thermodynamic temperature imparted locally to AlH_3 -1451 by irradiation with visible, ultraviolet, or gamma-rays, could easily exceed 60°C . which is probably above the threshold temperature for the onset of decomposition of the hydride. It would also be expected that the more energetic forms of radiation would increase this excitation. Although no quantitative data are available, qualitative observations indicate that ultraviolet light is more detrimental to stability than visible light, and that once the electron in the solid has been excited, the process is irreversible except perhaps at low temperatures (-15°C) over a long period of time. After excitation and attainment of more freedom by the electron, the bonds in the hydride lattice are more easily broken.

(U) As a semi-conductor, aluminum hydride possesses two bands, one a non-conducting band and the other a conduction band. At a given temperature the movement of electrons between the two bands is a steady state exchange. This equilibrium is changed by the presence of an electrical field, since electrons in the conduction band will couple with the electrical field, and the probability of their falling back to the non-conducting band is reduced, while motion in the reverse direction is unaffected.

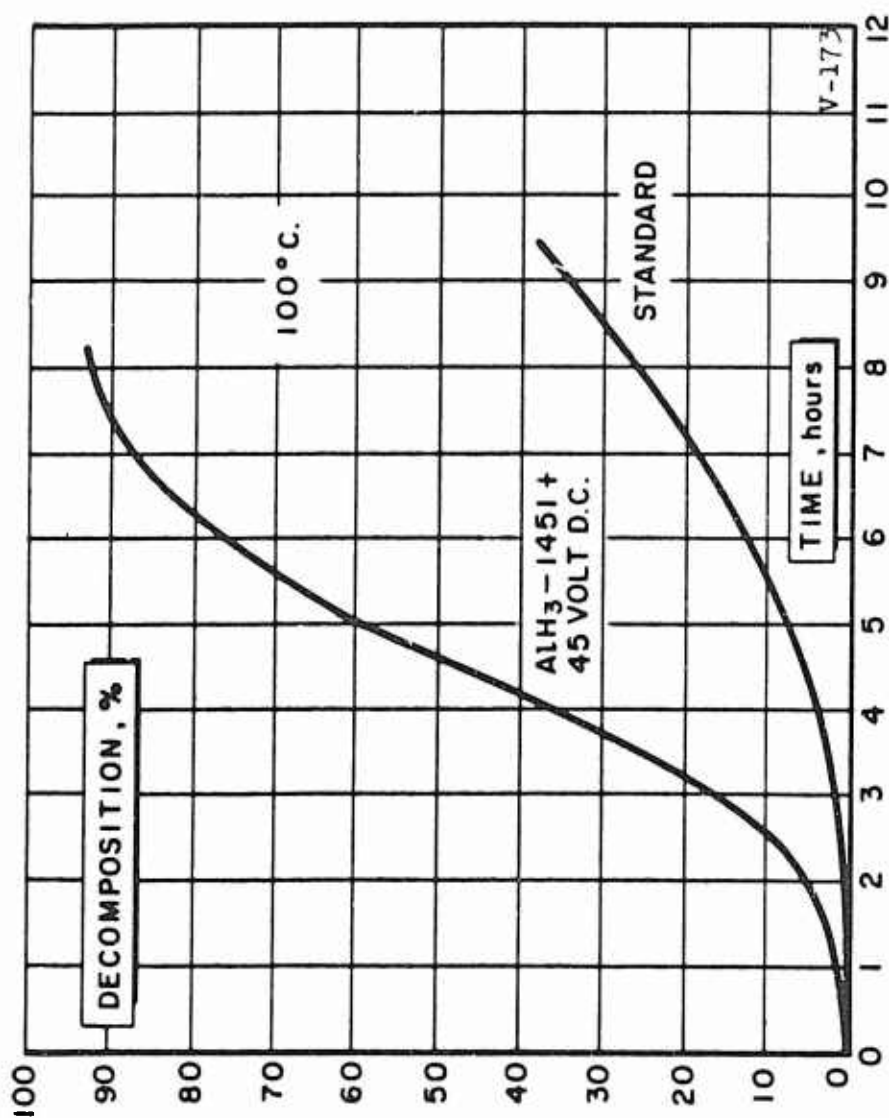
(U) An indication that the above process is operative is shown by the effect of an electrical field on the thermal stability of AlH_3 -1451 at elevated temperatures. Figure 13 illustrates the reduction in the length of the induction period of materials placed between an electrical field at 100°C . The presence of an electrical field increases the number of electrons in the conduction band to a value above that normally found at that temperature. This overpopulation of electrons in the conduction band, whether placed there by an electrical field or electromagnetic radiation, adds energy to the lattice and promotes a metastable condition conducive to initiating decomposition of the hydride. This factor alone would probably not be enough to give rise to the decomposition of AlH_3 -1451, but in combination with its thermodynamic instability and the unsymmetrical situation existing at the surface of the hydride, it does become very important.

b. Decomposition of Aluminum Hydride-1451 by the Loss of Surface-Terminated Hydrogens (U)

(U) A more complete understanding of the crystal structure of AlH_3 -1451 has led to a critical examination of the structure and bonding which exist at the surface of the hydride. If the mechanisms by which surface decomposition is initiated and continues to progress are understood, it should be possible to eliminate or greatly reduce the rate of decomposition of the hydride.

(U) The AlH_3 -1451 structure is a completely hydrogen-bridged three-dimensional network with aluminum atoms equidistant from each other at the points of a rhombohedral lattice and octahedrally bonded to six hydrogens. The latter are located off-center of the cell

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(u) Fig. 13 - Rate of Decomposition of Aluminum Hydride-1451 Neat and in Presence of an Electric Potential at 100°C.

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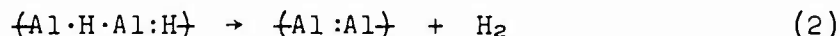
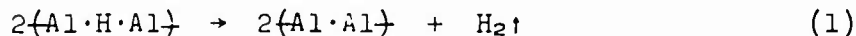
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edges. This configuration represents an "electron deficient" molecule, since there are more usable atomic orbits available than there are electrons to fill them. The result is a structure of three-centered, hydrogen-bridged bonds which consist of three orbitals occupied by two electrons in a manner similar to the hydrogen-bridged bonds in diborane. For purposes of accounting each hydrogen is assumed to contribute one electron, and each aluminum one-half electron to the orbital.

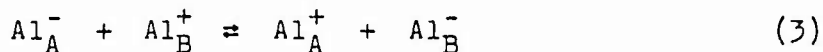
(U) In addition to the bridged hydrogens which make up the bulk of the structure, there are terminal hydrogens at the surface. The bond in this case is a "normal" localized sigma bond with aluminum and hydrogen each contributing one electron to the orbital.

(U) The initial decomposition reaction involving loss of hydrogen at the surface can be initiated by two reactions:

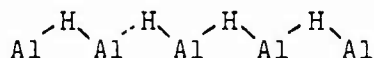


The first reaction denotes decomposition by loss of hydrogen from two adjacent hydrogen-bridges; the second results from reaction between a surface terminal hydrogen and a hydrogen bridge.

(U) Both reactions create anion vacancies which subsequently lead to active growth nuclei and further decomposition. In addition, a resonance effect, shown in Equation (3), which results from two aluminum atoms sharing one electron, Equation (1), probably contributes to the formation of color.



(U) The loss of hydrogen from the surface at highly exposed areas such as corners and fissures destroys the AlH_3 -1451 lattice and changes the bonding of the aluminum atoms. As a result, there is a shift in the electron density of the aluminum and hydrogen atoms. The hydrogen in the surface plane will move up and out of the plane to produce a sawtooth effect, as shown below, to compensate for the initial loss of hydrogen.



(U) These hydrogens are now less stable than those in the interior of the crystal and consequently may also be released as molecular hydrogen. The result is a slow loss of hydrogen at first (the initiation period) followed by an acceleration of decomposition as the stable nuclei formed during the induction period continue to grow.

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(U) These theoretical considerations of surface structure and bonding explain why surface treatments can reduce the rate of decomposition. This result is probably achieved by providing:

- (i) A more stable bonding situation for the orbitals of the aluminum at the surface.
- (ii) A reduction in the aluminum and especially hydrogen mobility at the surface resulting in a reduction in crystal stress.
- (iii) An electron sink by tying up the electrons freed by loss of hydrogen.

2. Magnesium Stabilization (U)

(C) The incorporation of magnesium into the crystal lattice of AlH_3 -1451 made by the batch process was found to significantly reduce the decomposition rate, although the type of solid solution formed was not known. More recently, however, it has been found that the effectiveness of magnesium stabilization also depends on the process used for making the hydride, and this has led to a more thorough study of the location and probable effect of magnesium in the aluminum hydride-1451 crystal lattice.

a. Location of Magnesium in the Hydride Lattice (U)

(C) X-Ray diffraction patterns of magnesium-doped hydride show no new lines, but do indicate a unit cell expansion which is proportional to the magnesium concentration. The absence of any new lines, which would be characteristic of the formation of a super-lattice or precipitation of a new phase, suggests the magnesium is randomly incorporated into the lattice.

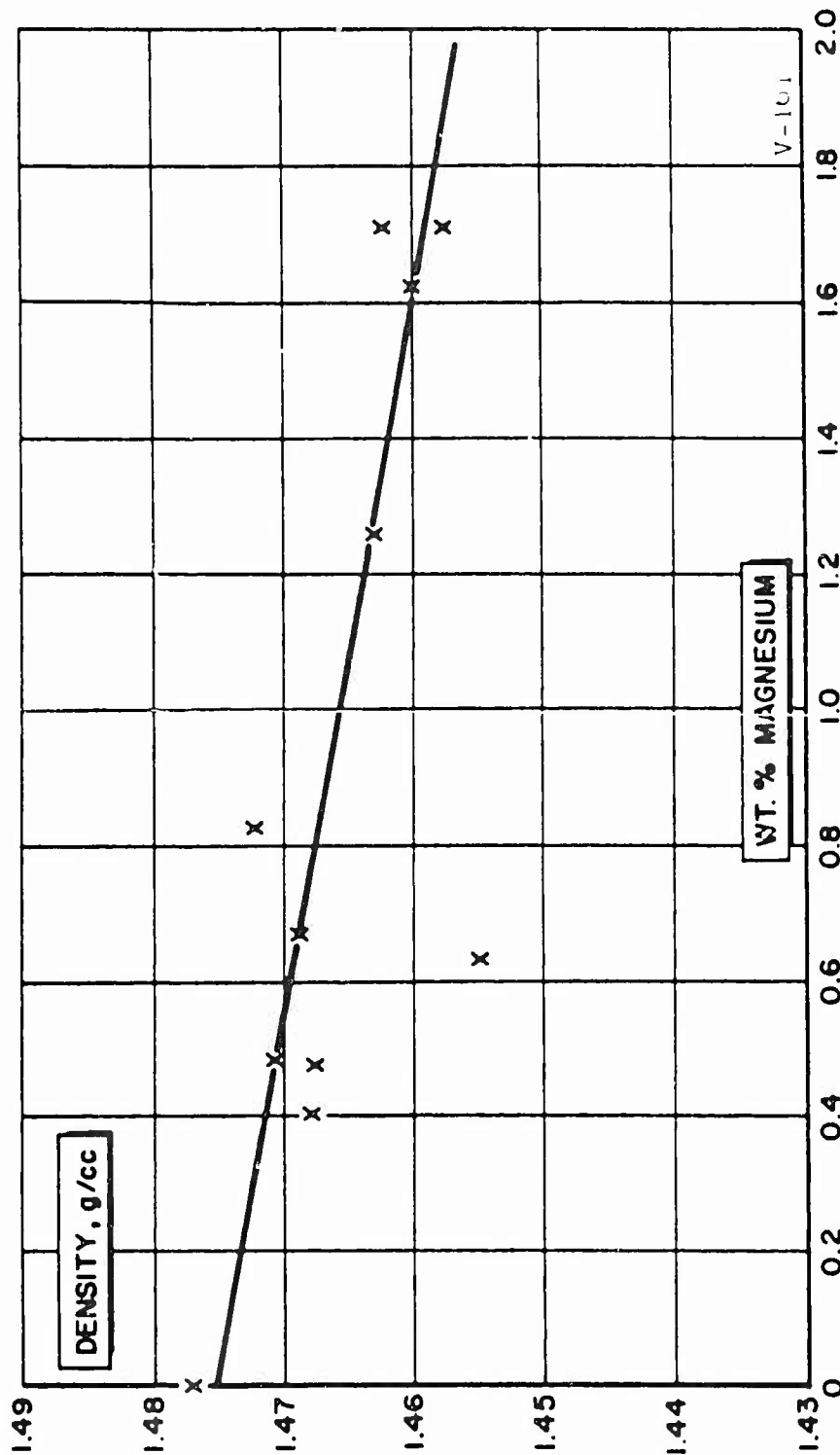
(C) Density measurements of magnesium-doped hydride have resulted in the location of magnesium in the hydride lattice. The density of a series of pilot plant samples containing varying concentrations of magnesium was measured by a helium densitometer. The measured densities were found to decrease as magnesium concentration increased as shown in Figure 14 and Table VII.

(C) Comparison of the calculated theoretical density with the measured density indicates that magnesium forms a substitutional solid solution. The measured and calculated densities and unit cell dimensions for each sample evaluated are given in Table VIII.

(U) The following formula was used to calculate the theoretical density:

$$D = \frac{nM}{AV}$$

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(1) Fig. 14 - Density of Aluminum Hydride-1451 as a Function of Magnesium Concentration

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D = Density

n = Number of moles per unit cell

M = Molecular weight

A = Avogadro's number

V = Volume of unit cell ($A^2c \sqrt{3}/2$
for hexagonal system)

A density of 1.477 was measured for the macrocrystalline sample compared to 1.4768 g./cc. calculated using the above formula and measured unit cell dimensions given in Table VIII.

Table VII

(U) Summary of Density Measurements of Pilot Plant Samples

<u>Sample Number</u>	<u>Wt. % Mg</u>	<u>Measured Density, g./cc.</u>
02025A	None	1.477
04035A	None	1.473
QX 018	0.41	1.468
01286	0.48	1.468
QX 019	0.51	1.471
01206	0.63	1.455
01216	0.67	1.469
01316	0.81	1.472
05106	1.26	1.463
05066	1.62	1.460
05195A	1.70	1.462
05136	1.71	1.458

Table VIII

(U) Comparison of Theoretical and Measured Densities

<u>Hydride Type</u>	<u>Cell Dimensions, Å</u> <u>a</u> <u>c</u>	<u>Density, g./cc.</u>			
		<u>Theoretical</u>			<u>Measured</u>
		<u>Substitu- tional</u>	<u>Inter- stitial</u>	<u>Normal</u>	
Macrocrystal- line	4.4493 ± 0.005	11.8037 ± 0.0024		1.4768	1.477
Magnesium- doped (1.62% Mg)	4.4609 ± 0.005	11.8428 ± 0.0016	1.4617 1.4607 ^a	1.4884 1.4904 ^a	1.460

^aCorrected for valence.

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(C) The theoretical density of the solid solution formed by the addition of magnesium was calculated assuming:

- (i) The magnesium is substituting at random for an aluminum atom in the crystal lattice forming a substitutional solid solution.
- (ii) The magnesium is accommodated in the interstices between the aluminum atoms forming an interstitial solid solution.

(C) Because no information is available to indicate maintenance of crystal neutrality when doping the crystal with magnesium, the densities were calculated by two different methods:

- (i) Ignoring crystal neutrality, and
- (ii) Correcting the hydrogen value for the amount of magnesium present.

The differences in density resulting from the valency correction are small as shown in Table VIII.

(C) A comparison of the measured value (1.460 g./cc.) with the calculated densities assuming substitution (1.4617 and 1.4607 g./cc) or interstitial (1.4884 and 1.4904 g./cc.) magnesium placement indicates the magnesium-doped lattice represents a substitutional solid solution phase. Excellent agreement was obtained between density and magnesium concentration as shown in Figure 14. The density of samples prepared by different processing techniques was also determined. Table IX summarizes the measured and calculated density values for several lots. The density of the samples containing magnesium was calculated on the assumption that the magnesium is forming a substitutional solid solution. The good agreement between measured and calculated density values does show the magnesium is entering the lattice substitutionally, regardless of the processing technique used to prepare the material. Therefore, other factors must be responsible for the observed differences in thermal stability noted in Section A.1.b.

b. Process Effects (U)

(C) The incorporation of magnesium into the crystal lattice of AlH_3 -1451 has been shown to significantly reduce the rate of decomposition. However, recent data indicate that the role magnesium plays in the stabilization of the hydride is much more complex than originally thought.

(C) It is now known, as a result of process studies, that incorporation of magnesium, per se, is not sufficient to guarantee stabilization of the hydride. The effect of process changes on stability is discussed in detail in Section A.1.b. These studies

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have shown the macroproperties, such as lattice expansion, magnesium concentration, particle size, chloride content, etc., are not sufficient to predict stabilization.

Table IX

(U) Effect of Preparative Method on Magnesium Incorporation

Sample No.	Preparative Method	% Mg	Density		Diff.
			Meas.	Calcd.	
04035A	Pilot Plant	None	1.473	1.4758	0.0028
05106	Pilot Plant	1.26	1.463	1.4629	0.0001
05136	Pilot Plant	1.71	1.458	1.4611	0.0031
05195A	Pilot Plant	1.70	1.462	1.4637	0.0017
9974-19B	Lab Batch	None	1.442	1.4766	0.0346
9974-19C	Lab Continuous	None	1.466	1.4767	0.0107
9569-16-1	Lab Batch	1.92	1.461	1.4577	0.0033
655-166AB	Mini-plant Continuous	1.83	1.456	1.4610	0.0050

(C) It has been shown by many different techniques that the decomposition of the hydride occurs predominantly at the surface. The lengthening of the induction period or stabilization caused by the incorporation of magnesium should, therefore, be considered in terms of changes which occur at the surface of the hydride due to the incorporation of magnesium. It is known from structure studies of AlH_3 -1451 that different crystal planes (faces) will possess different populations of aluminum and hydrogen atoms at the surface. It may be possible that magnesium incorporation must be accompanied by certain crystal faces in order to cause stabilization of the hydride.

(C) Assuming this hypothesis is correct, a change in preparative process could easily change the morphology of the AlH_3 -1451 crystals. Hence, stabilization is not observed in the laboratory continuous crystallization process, even though magnesium is incorporated, because the crystal faces represent different planes of atoms.

(C) Depending upon which crystal face is present, surface terminal hydrogens may be exposed, and, when lost, contribute to the initiation of decomposition. Incorporation of magnesium, since it could participate in only a maximum of four three-centered bonds, could very easily prevent exposing these terminal hydrogens at the surface. This viewpoint would then aid in explaining the beneficial effect of adding magnesium substitutionally to the hydride lattice.

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(C) The "aging" phenomenon associated with magnesium-doped hydride as discussed in Section B.2.b. also appears to be related to surface conditions. All of these studies have generated data which strongly suggest that magnesium stabilization, although primarily an intramolecular change, should be considered a surface phenomenon.

3. Stabilization of Aluminum Hydride-1451 by Surface Treatment with Diphenylacetylene (DPA) (C)

(C) A number of compounds containing phenyl groups were screened to establish their effectiveness as stabilizers for AlH_3 -1451; of these, diphenylacetylene (DPA) was found to be the most effective.

a. Initial Studies of DPA Treatment (U)

(C) Work during the first part of the year consisted of treating AlH_3 -1451 samples with DPA and determining their increase in thermal stability by the Taliani method. The favorable results obtained from these experiments led to a thorough investigation of process parameters to find conditions which produced maximum stability.

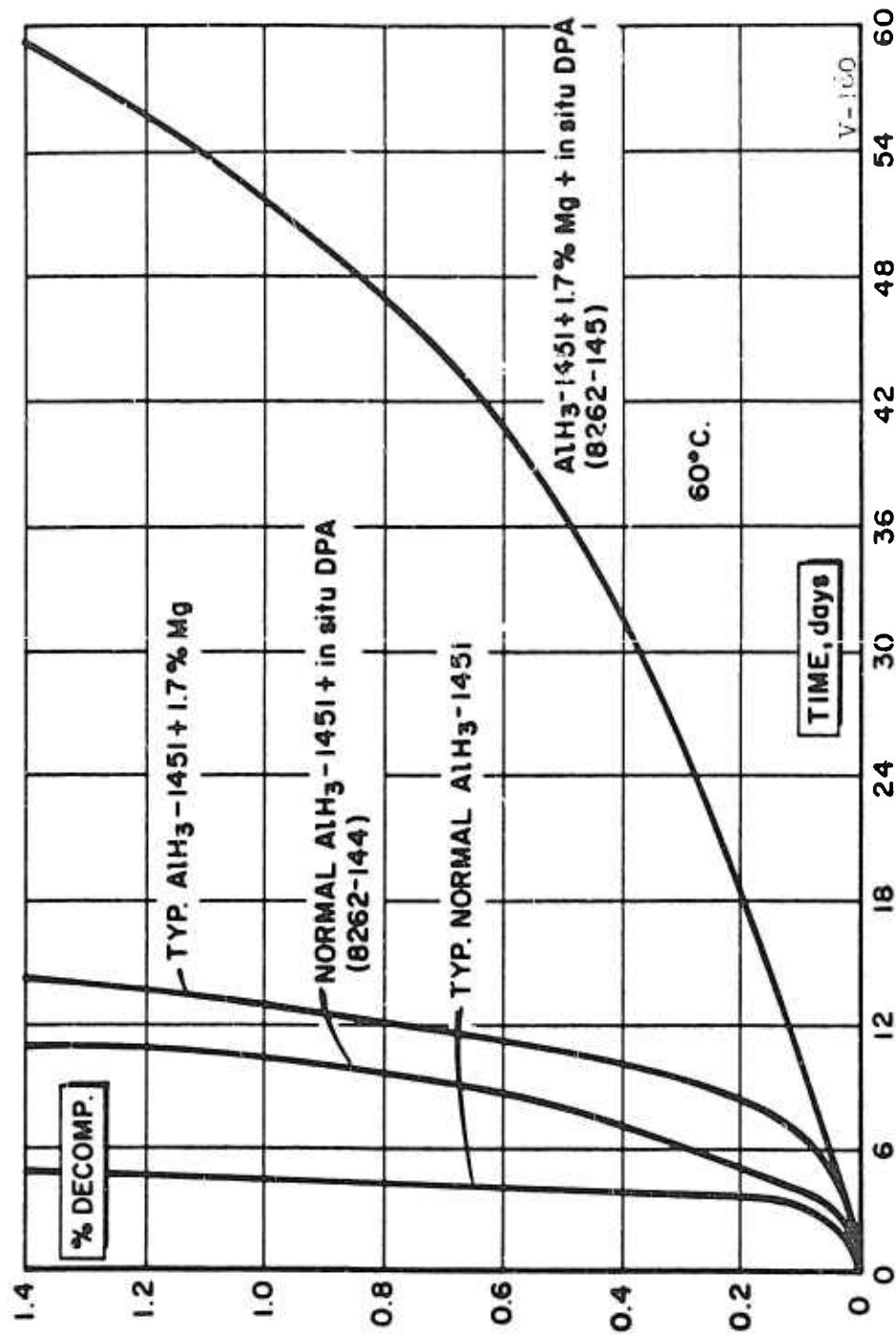
(C) The first samples tested were a 50-50 wt. % mixture of AlH_3 -1451 and DPA. A magnesium-doped hydride sample (1.65%) required 115 days at 60°C . to reach 1% decomposition, compared to 29 days for the reference under the same conditions; thus, a 3.5-fold improvement in thermal stability was attained. The same sample at 100°C . decomposed only 10% in the first 25 days and only 2.2% in the next 85 days. The presence of AlH_3 -1451 in the sample which remained was confirmed by X-ray analysis. These results clearly indicated the DPA was an effective stabilizer, and more practical means of treatment were explored.

(U) Refinements in the procedure included the use of a pressure transducer instead of a mercury manometer, thereby eliminating any detrimental effect due to mercury, and the use of a wash treatment technique which produced uniform low concentrations of DPA on the surface of the hydride crystals.

(C) The treatment of magnesium-doped AlH_3 -1451 with DPA was more effective than when applied to conventional AlH_3 -1451, and even greater increases in stability resulted from DPA treatment of the sample prior to recovery and drying. This latter technique is referred to in the remainder of the report as in situ treatment.

(C) Figure 15 shows the increase in stability realized by the in situ DPA treatment of typical conventional and magnesium-doped hydride samples made by the batch process. The conventional samples show approximately a twofold improvement while the magnesium-doped hydride shows a fourfold increase in the time required to reach 1% decomposition at 60°C . The elemental analysis of these two samples is given in Table X.

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(c) Fig. 15 - Comparison of Effectiveness of DPA on Normal and Magnesium-Doped in situ Treated Hydride

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Table X

(C) Elemental Analysis of DPA-Treated
Aluminum Hydride-1451

Element	% Composition	
	Normal	Mg-Doped
C	2.9	1.3
H	10.0	9.9
Al	86.2	85.8
Mg	--	1.7
Cl	0.3	0.5
Li	0.2	0.5

b. Process Parameters Influencing Stabilization of Aluminum
Hydride-1451 by DPA (C)

(C) The initial work proved conclusively that when batch aluminum hydride-1451 was surface treated with diphenylacetylene (DPA) its thermal stability was greatly improved. The next phase of the work consisted of defining limits and developing methods and techniques for acquiring maximum stabilization of the hydride with DPA.

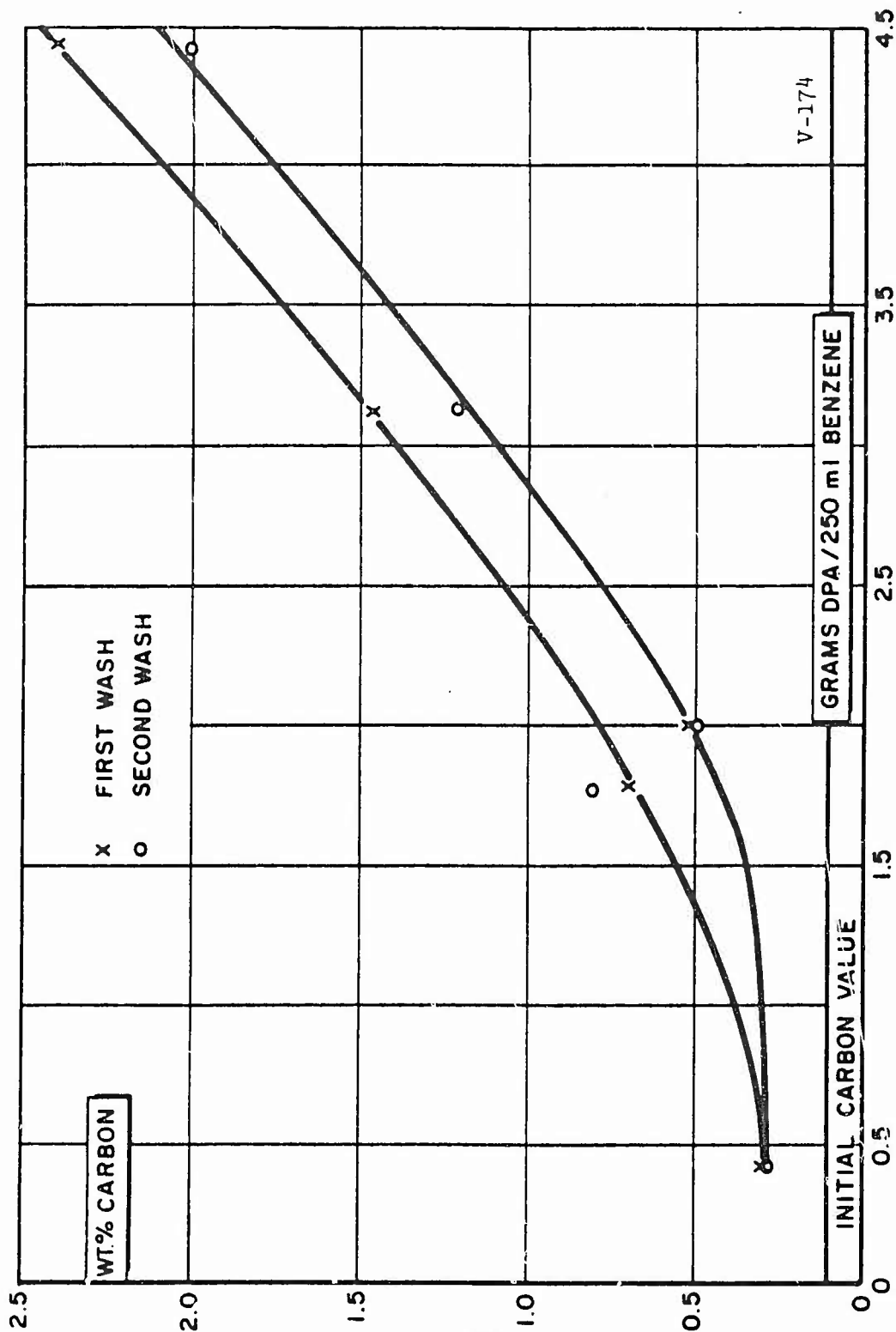
(1) Coating Techniques (U)

(C) Experiments with different concentrations of DPA in the benzene wash solution showed that no appreciable increase in the thermal stability of standard AlH_3 -1451 was obtained with 50 mg. of DPA/250 ml. of benzene. When the concentration was increased fivefold to 250 mg. of DPA/250 ml. of benzene, a significant improvement in thermal stability resulted, the samples requiring 8 to 20 days before reaching 1% decomposition at 60°C.

(C) A study was also made to determine the optimum concentration of DPA necessary for stabilization of AlH_3 -1451. Samples of normal and magnesium-doped AlH_3 -1451 were washed with 4.47, 3.12, 1.78, and 0.445 g. of DPA/250 ml. of benzene. The results, illustrated in Figure 16, show the wt. % carbon or DPA concentration on the surface of the hydride increases as the concentration of the wash solution increases. Hence, the method is applicable for control of the concentration of DPA placed on the surface. By using this technique there is very little change in the physical characteristics of the hydride except for perhaps a slight change in color and flow characteristics. The relationship between wt. % carbon and concentration of the DPA wash solution, shown in Figure 16, is generally true for both normal and magnesium-doped hydride lots, although it has been noted that magnesium-doped hydride tends to remove a little less of the DPA from solution.

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(U) Fig. 16 - Relationship between Weight Percent Carbon and Concentration of Wash Solution

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(C) The same wash solutions were also used again without additional treatment to determine if the wash solution could be reused. The results obtained from a series of samples using the same wash solutions a second time is also shown in Figure 16. There was a tendency to deposit less DPA on the surface of the hydride the second time as would be expected, if the concentration of the solution had decreased as a result of the amount removed during the first wash. Therefore, it appears probable that a DPA wash solution can be used several times if additional DPA is added to make up for the amount removed due to the prior wash. The coating technique described above, however, has not been satisfactory in treating product prepared by the continuous process as discussed in Section A.1.c.

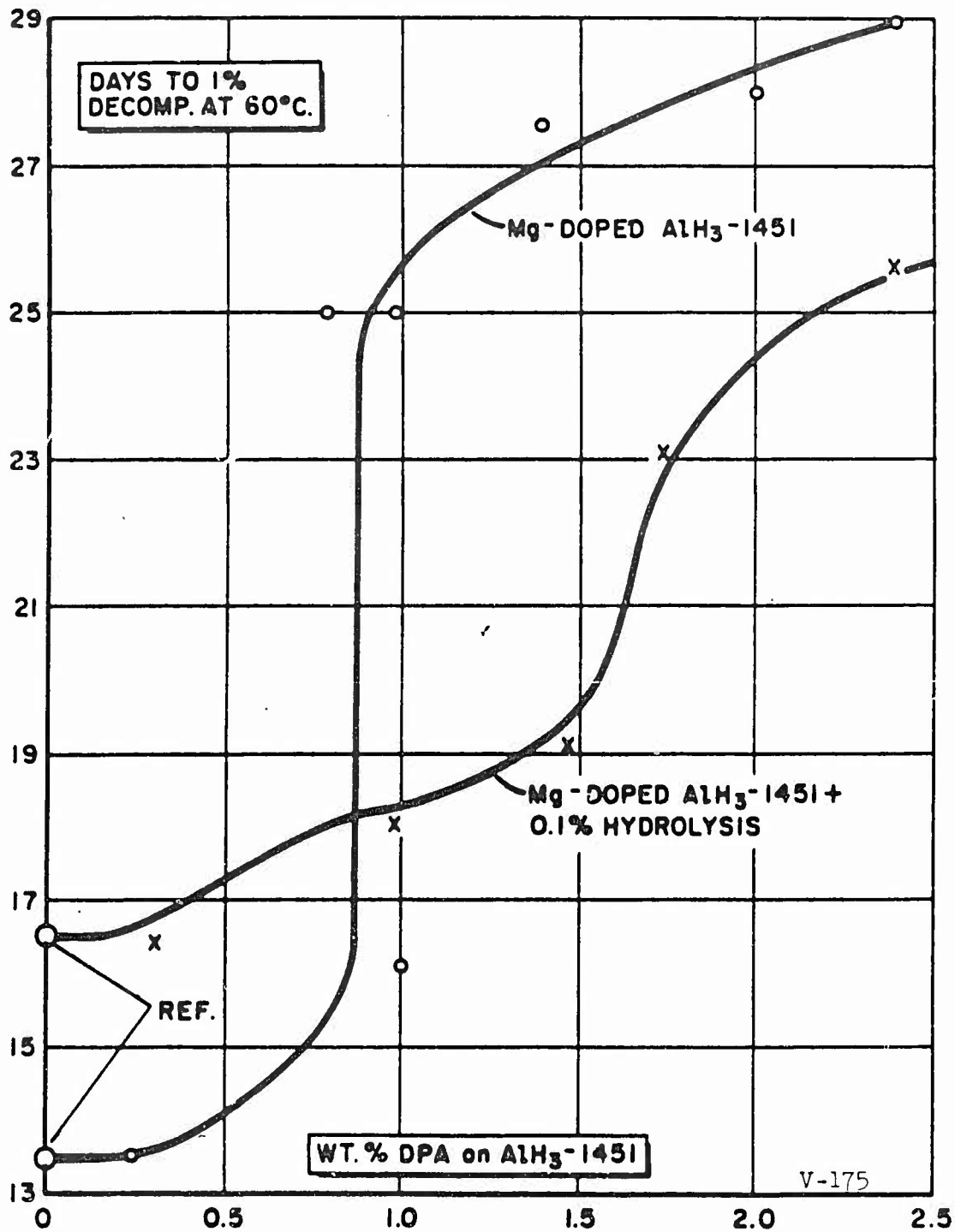
(C) The relationship between stability, in days to reach 1% decomposition at 60°C., and percent DPA is plotted in Figure 17. This relationship indicates that the most useful concentration of DPA on the surface of the hydride is probably between 1.0% and 2.5%. However, the DPA has a definite tendency to sublime away from the surface of the hydride at accelerated test temperatures suggesting that concentrations much lower than these may suffice at ambient temperature. The higher concentrations of DPA gave only marginal improvements in stability. The optimum concentration of DPA in a wash-treatment solution appears to be one containing 2.5 g. of DPA/250 ml. of benzene.

(C) The same lot of magnesium-doped material was surface hydrolyzed 0.1% prior to DPA treatment. As illustrated in Figure 17, the hydrolyzed magnesium-doped sample did not respond to DPA treatment nearly as well as the original magnesium-doped lot. Much larger concentrations of DPA were necessary to obtain the same degree of stabilization. Therefore, it appears that the condition of the hydride surface is important prior to DPA treatment. Data also obtained from a magnesium-doped AlH_3 -1451 sample (1.73% Mg), which was washed with a solution of 2 g. of DPA/250 ml. of benzene immediately after preparation and before drying, produced a very stable sample, requiring 51 days to reach 1% decomposition at 60°C., as shown in Figure 15. Additional experiments with the in situ technique confirmed the above results (Figure 18). The magnesium-doped hydride usually exhibited a reproducible fourfold increase in stability over the untreated material and demonstrated excellent stability in propellant formulations (see Section E). In contrast, samples treated after recovery and drying generally showed only a twofold improvement in thermal stability, and essentially no improvement in propellant formulations (see Section E).

(C) These data suggest that optimum stabilization is probably obtained from DPA treatment of the hydride prior to recovery and drying from the crystallizing solution. This seems logical since an aluminum oxide coating on the surface of the hydride could act as a barrier between the surface, where decomposition initiates, and the DPA stabilizer.

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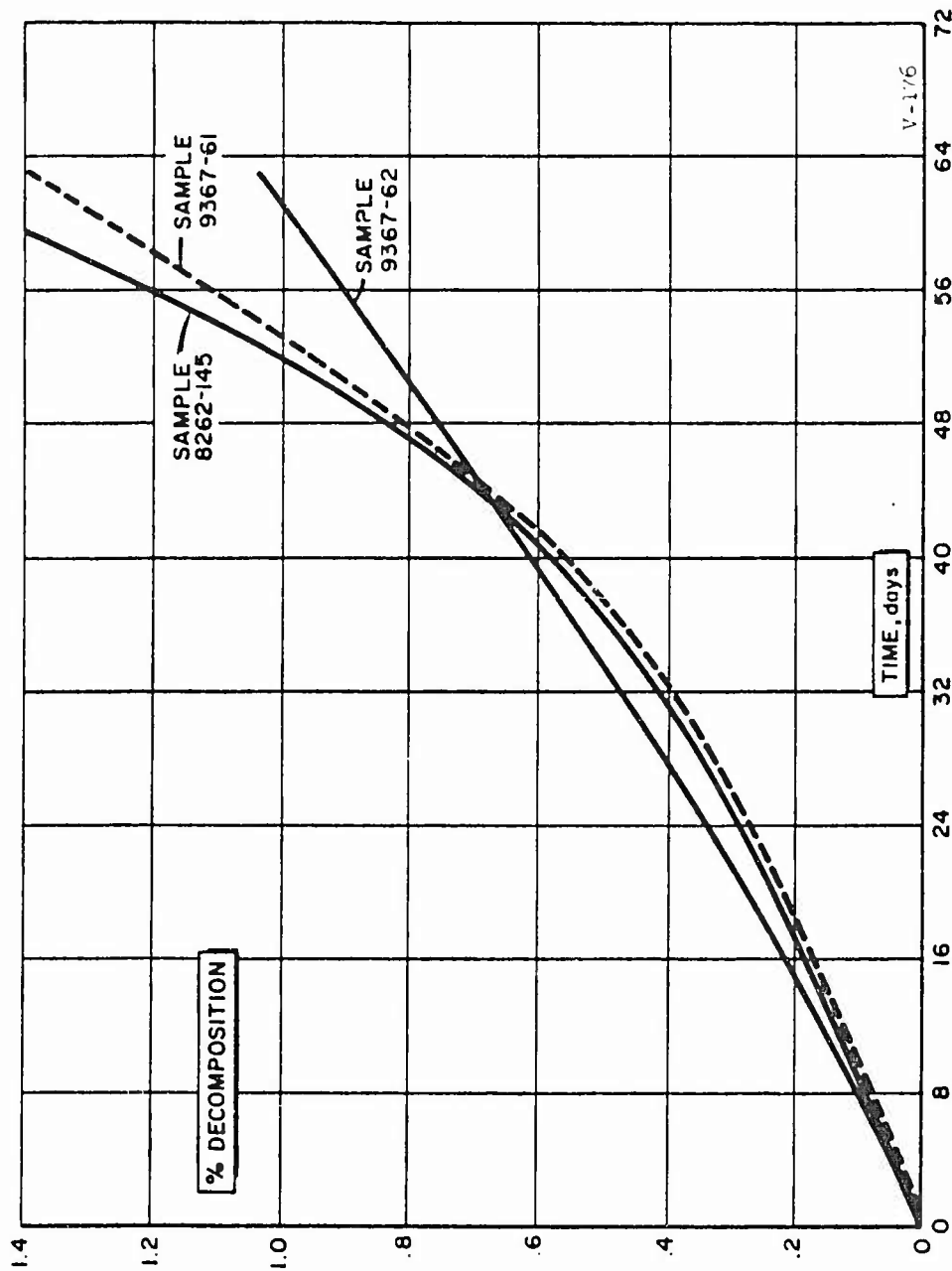
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(C) Fig. 17 - Relationship between Stabilization and Weight Percent DPA for Magnesium-Doped and Surface Hydrolyzed Magnesium-Doped Aluminum Hydride-1451 after Preparation

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(C) Fig. 18 - Decomposition Rates of Three Magnesium-Doped, in situ DPA-Treated Aluminum Hydride-1451 Samples

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(C) An evaluation of the same sample at 100°C., however, exhibited very little improvement in thermal stability. This suggests that either larger quantities of DPA are necessary to stabilize the material at higher temperatures or the small amounts of DPA present quickly sublime or vaporize away from the surface of the hydride resulting in loss of stabilization.

(C) The DPA treatment of two standard AlH₃-1451 samples at 25°C. and 80°C. did not result in any difference in thermal stability, and from this experiment it was concluded that treatment temperature was not an important factor.

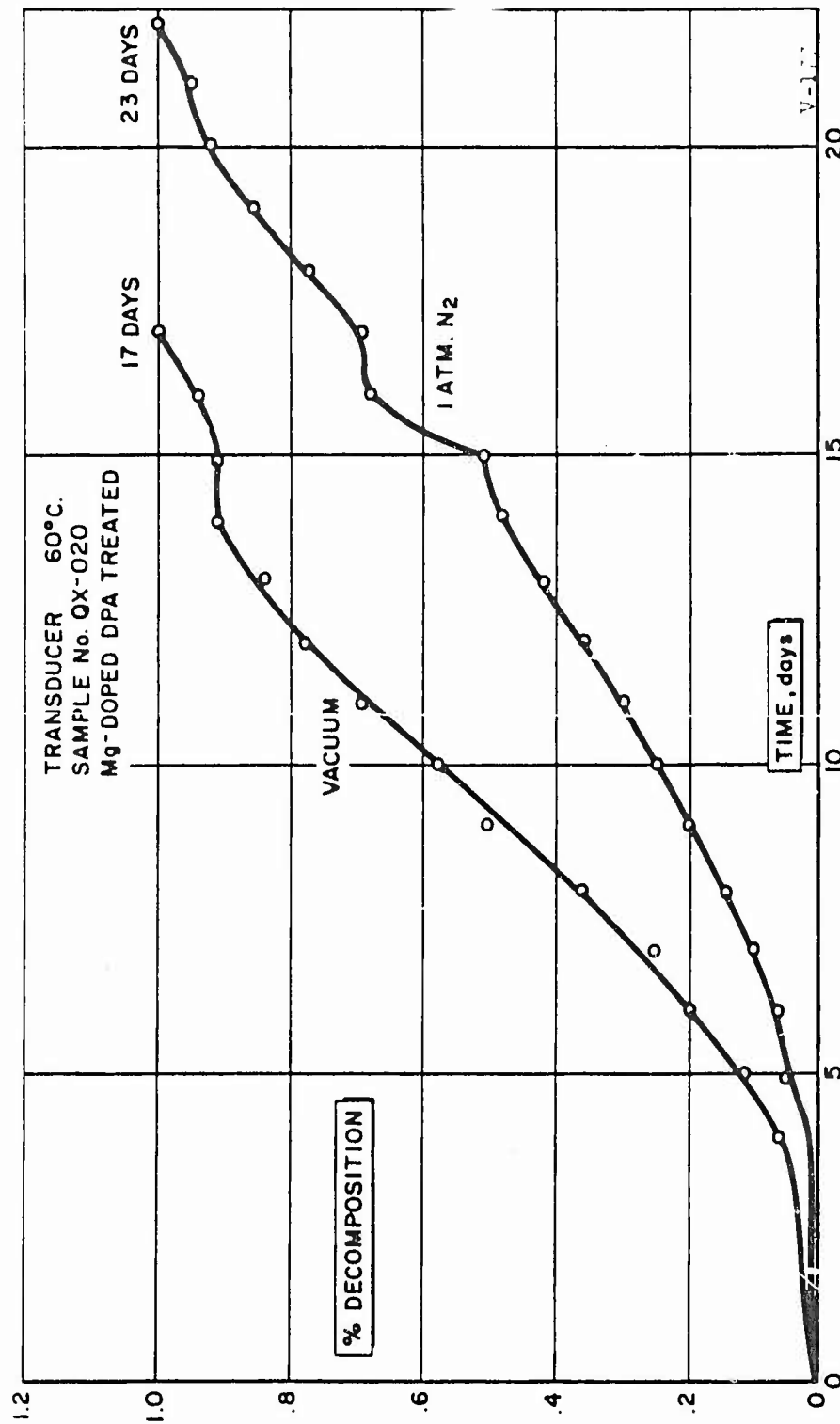
(2) Loss of DPA by Sublimation (U)

(C) Examination of eight different lots of hydride has confirmed original observations suggesting that 1-2 wt. % DPA is necessary for the stabilization of AlH₃-1451. However, observation of samples on test has shown that the DPA often sublimates away from the surface of the hydride, condensing on the cooler parts of the accelerated test apparatus. DPA melts at 57°C. to 63.5°C., depending upon purity, and can have an appreciable vapor pressure at 60°C. At lower temperatures this is not expected to be a problem.

(C) The resublimed crystals mentioned above have been identified as DPA by X-ray diffraction analysis. The effectiveness of DPA cannot be definitely established because the elevated temperatures used for accelerated testing of the thermal stability of AlH₃-1451 are also sufficient to sublime the stabilizer away from the hydride surface. Hence, further investigation of this problem appeared necessary. The decomposition rates measured by a pressure transducer from DPA-treated samples at 60°C. under vacuum are greater than those obtained under an atmosphere of nitrogen as shown in Figure 19. These differences in decomposition rates are attributed to the differences in rate of DPA sublimation away from the hydride surface. Elemental analysis of DPA-treated AlH₃-1451, before and after testing, has also indicated an appreciable reduction in carbon content during testing. Twenty-seven samples of AlH₃-1451, which possessed a carbon concentration before testing ranging from 0.5-2.4%, were found to contain an average content of 0.54% with a standard deviation of 0.12% after testing. A slight correlation seems to exist between the amount of DPA initially present and the amount present after testing, as the samples with higher initial carbon values, as a rule, gave higher final carbon values.

(C) Laboratory samples in situ treated with DPA and evaluated at 60°C. reached 1% decomposition in approximately 50-60 days. If a 50-50 wt. % mixture of AlH₃-1451 and DPA is used, the hydride will require more than 100 days to reach 1% decomposition. This suggests that if, the DPA did not sublime away from the surface of the hydride during accelerated testing at 60°C.,

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(C) Fig. 19 - Effect of Vacuum versus Nitrogen on Decomposition Rate of a DPA-Treated Sample of Aluminum Hydride-1451

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greater stabilities would perhaps be observed from the samples with a maximum possible stability being near 100 days. Hence, the fugacity of DPA may be the controlling factor in the stabilization of AlH_3 -1451 at elevated temperatures.

(3) Attempts to Reduce Sublimation Rate (U)

(a) Reduction in Test Temperature (U)

(U) There is often a marked difference in sublimation rate as a material changes state from liquid to solid. On this basis, it was decided to evaluate DPA-treated hydride at a temperature below its melting point of $57^\circ\text{-}63.5^\circ\text{C}$.

(C) To determine if the effectiveness of the DPA-treated material increased as the temperature decreased, two other hydride lots were evaluated for comparison purposes. They were a normal macrocrystalline sample (02025A), and an "aged" magnesium-doped sample (8262-1031-15). The temperature of 50°C . was chosen in an effort to obtain data as quickly as possible.

(C) Figure 20 shows the decomposition rate measured at 60°C . for the three different lots. The in situ DPA-treated pilot plant sample exhibited a stability intermediate between the normal macrocrystalline and the "aged" magnesium-doped material. The results obtained from evaluation of these three lots of hydride at 50°C . are depicted in Figure 21. The relative stability of the three samples did not change. Hence, it is concluded that a reduction of 10°C . in test temperature to below the melting point of DPA did not increase the effectiveness of the DPA.

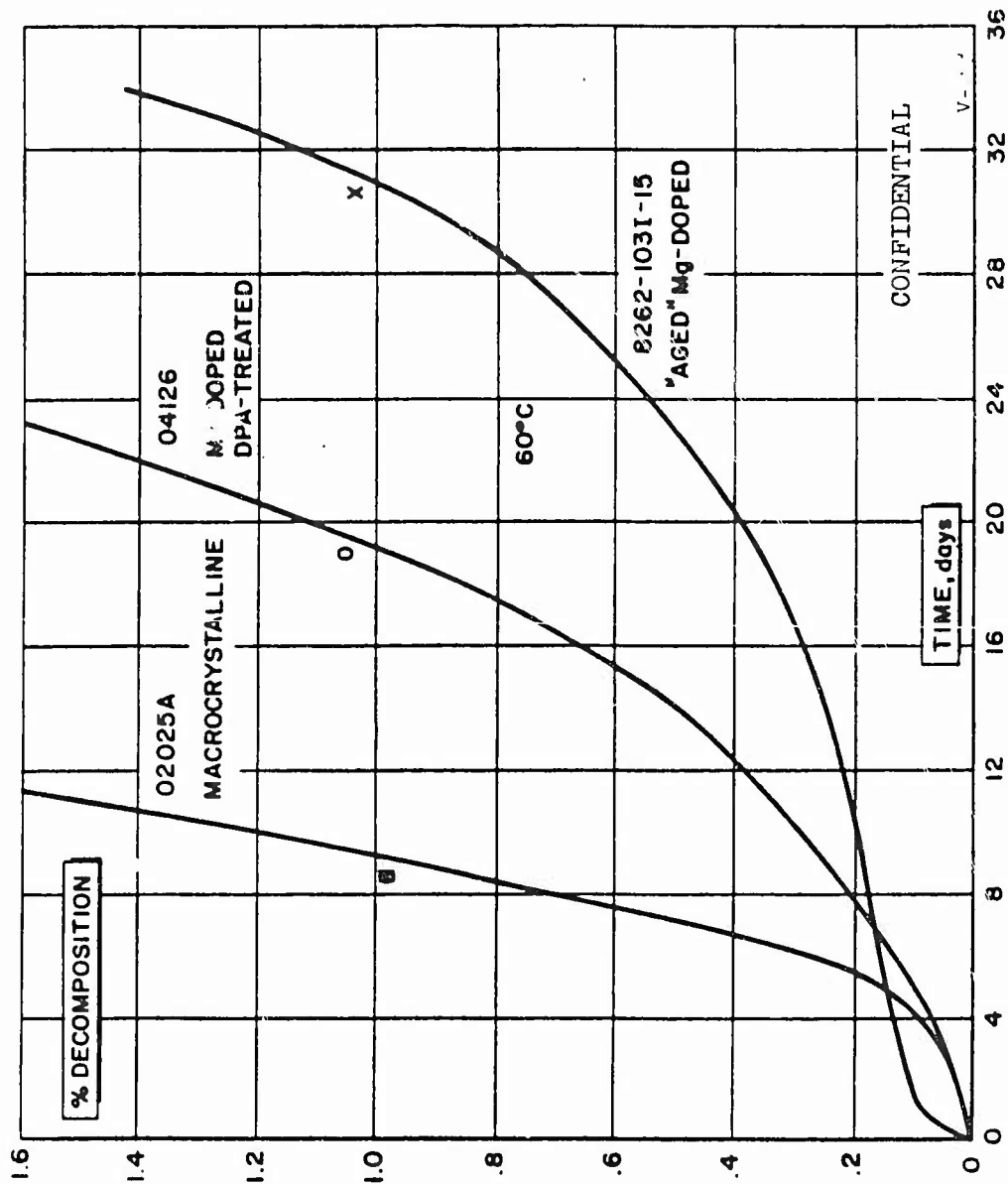
(b) Pelletized DPA-Treated Material (U)

(C) Another attempt at reducing the rate of sublimation of the DPA was by pelletizing the AlH_3 -1451. The DPA-treated hydride was pelletized using 0.1% DPA as binder and an infrared lamp to melt the DPA. Evaluation of the $1/4$ " pellets indicated only a 6 to 7 day increase in stability at 60°C . compared to the standard (19 days to 1% decomposition). This increase could be accounted for by the increased concentration of DPA present. Extremely large platelets of DPA crystals were still observed to form on the cooler parts of the apparatus indicating sublimation was still occurring at a substantial rate.

4. Mechanism of DPA Stabilization (U)

(C) Having conclusively shown that DPA stabilizes AlH_3 -1451 particularly by the in situ treatment of the hydride, it was necessary to investigate the mechanism of stabilization. Experiments were therefore designed to determine if the improvement in stability was due to a chemical reaction, chemical adsorption, and/or physical adsorption.

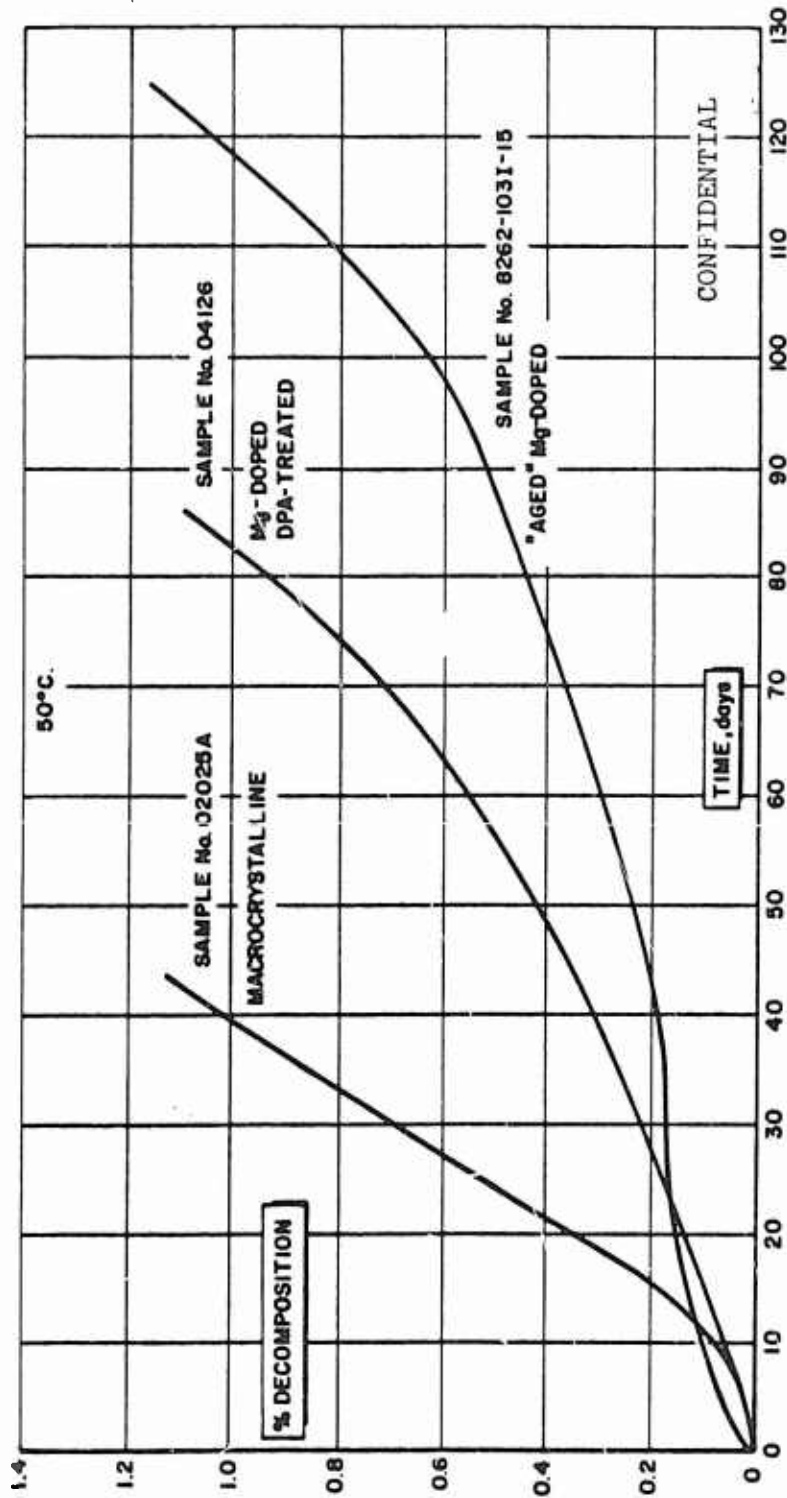
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(U) Fig. 2 - Decomposition of various Types of Hydride at 60°C.

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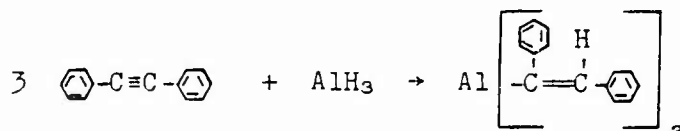


(U) Fig. 21 - Decomposition of Various Types of Hydride at 50°C.

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(C) The most likely reaction to occur would be the addition of aluminum hydride across the triple bond of DPA. This could proceed in a stepwise manner until all the hydrogens are reacted as shown in the following equation:



(C) The reactivity of aluminum hydride with diphenylacetylene in solution was examined to determine if this reaction takes place. If no reaction occurred between the two solutions, it would be very strong evidence that the DPA would not react with the less reactive form of aluminum hydride, AlH₃-1451. No visible reaction was observed when two millimoles of AlH₃ were added to six millimoles of DPA in 75 ml. of diethyl ether. After removing the solvent at a reduced pressure, X-ray analysis of the remaining solid showed only DPA to be present. The solid showed hydride activity with water, indicating the presence of unreacted aluminum hydride. It was concluded from the above results that the solid product consisted of a mixture of DPA and aluminum hydride, and that no reaction had occurred. This result is supported by the work of Smith et al. (6), who found no evidence for the reduction of the triple bond in hexyne-1 by lithium aluminum hydride at room temperatures. These data do not rule out the possibility of a reaction during decomposition, where extremely reactive radicals may be generated, but do show that the stabilization is not a result of an initial reaction between the two materials.

(C) The possibility that stabilization of AlH₃-1451 occurs by either chem-adsorption and/or by the deposition of a thin layer of DPA in intimate contact with the AlH₃-1451 crystals was studied. Ten grams of Lot No. QX 020 magnesium-doped AlH₃-1451, obtained from the Dow Pilot Plant, was washed with a solution containing 5 g. of DPA in 250 ml. of benzene. After drying, a portion of the sample was analyzed for carbon content to determine the amount of DPA remaining on the AlH₃-1451 and was examined at 60°C. on the Taliani to determine its stability.

(C) The remainder of the DPA-treated AlH₃-1451 was washed with 100 ml. of fresh benzene to determine the quantity of DPA removed by a single solvent wash. The same analyses as for the original DPA-treated hydride were carried out; in addition the benzene wash was analyzed for DPA by means of gas-liquid chromatography. This procedure was repeated four times with the results shown in Table XI.

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Table XI

(C) Effect of Solvent Wash on Stability and DPA Concentration of DPA-Treated Aluminum Hydride-1451 (Lot QX-020)

Sample	% C	% H	% DPA on Sample (Based on % C)	% DPA (Benzene Wash)	Decomp. Days to 1% (60°C. Taliani)
QX-020	<0.1	10.02	0	--	14
DPA-Treated QX-020	1.74	9.99	1.84	--	24
Wash 1	0.28	9.94	0.3	0.114	13
Wash 2	0.29	10.01	0.3	0.005	13
Wash 3	0.30	9.98	0.3	0.0005	14
Wash 4	0.16	9.92	0.2	<0.0005	14
Wash 5	0.20	9.90	0.2	<0.0005	13

(C) The data indicate the after-treatment with DPA doubles the stability of the AlH_3 -1451, but show that 85% or more of the DPA deposited by the treatment can be removed by a single fresh solvent wash. Practically no further change resulted from additional washing as shown by a constant carbon content (within experimental error), low DPA content in the benzene washes, and a constant stability equal to that obtained before DPA treatment.

(C) Since the in situ treatment of AlH_3 -1451 with DPA resulted in increased stability, a Dow Pilot Plant magnesium-doped, in situ DPA-treated AlH_3 -1451 sample (Lot 04126) was also examined. Its stability, however, was less than expected for unknown reasons, since it required approximately the same time to reach 1% decomposition as material which was DPA-treated after drying. The sample was, as before, treated with a single fresh benzene wash, and its carbon and hydrogen content and stability at 60°C. determined. The same effect was found as with the previous sample (Lot QX-020) which was not in situ treated. The DPA content decreased from 1.44% to 0.2% and the stability was lowered from 22 days to 11 days. A laboratory sample, however, containing no magnesium, but in situ treated with 1.73% DPA, required 20 days to reach 1% at 60°C. by the Taliani test. This sample, after a single fresh benzene wash, contained 0.85% DPA and its stability decreased to only 12 days, which is much better than the 3-6 days expected for the same untreated hydride.

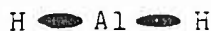
(C) In summary, the experimental evidence strongly suggests that no reaction occurs between the AlH_3 -1451 and the DPA on the hydride surface for the following reasons:

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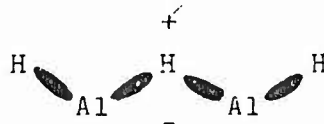
- (i) DPA does not react chemically with aluminum hydride in solution.
- (ii) A single fresh solvent wash greatly reduces the DPA content of the AlH_3 -1451 and its stability.
- (iii) Stabilization is a function of DPA content on the surface far in excess of that necessary for a few monomolecular layers.
- (iv) The DPA readily sublimes from the hydride surface at elevated test temperatures.

(C) Experimental results demonstrating that the in situ treatment of the hydride with DPA is much better than treating after recovery and drying strongly imply chem-adsorption and that a very intimate contact between the DPA and the hydride surface is necessary to obtain maximum stabilization. Physical adsorption would not give an electronic couple which appears desirable. A chem-adsorption couple would be weak in nature. It is known that in certain instances hydrogen bonding can occur with unsaturated compounds (7,8). Considering the structural aspects of AlH_3 -1451 as previously discussed (B.l.b.), the concept of weak hydrogen bonding or weak Lewis acid-base reaction could explain how an electronic couple is formed between DPA and AlH_3 -1451.

(C) The sawtooth surface that probably exists in AlH_3 -1451 gives rise to a rather unique situation. The shape of the electron density plot in the bonding of a H-Al-H linkage in the body of the crystal would have a high degree of symmetry around the Al atom. In the case of the H-Al-H linkage at the surface this is probably not true. The electron density plot of the H-Al-H linkage in the crystal, though not completely linear, resembles the following:



The non-linear or surface H-Al-H linkage differs as shown:



This dissymmetry in the electron clouds would give rise to an effective region acting as a very small negative charge in the interior. A region acting like a positive charge on the hydrogen could be attracted to the unsaturated linkage in the DPA ($-\text{C}\equiv\text{C}-$) and form a weak adduct. This adduct is weakly bonded because the effective positive charge on the hydrogen would have only a very weak electrostatic attraction for the effective negative charge of the delocalized bond in DPA.

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(C) An electronic coupling could also be formed between DPA and the AlH_3 -1451 by means of the aluminum atoms on the surface acting as Lewis acids. Since the triple bond in DPA can act as a Lewis base (7,8), a weak adduct could be formed between the empty orbital of the aluminum and the electron-rich orbital of the delocalized bonds in DPA.

(C) Either or both of these two situations could provide electronic couples which act like bridges for electrons to be accepted or donated by the AlH_3 -1451. This mechanism provides for an excess electron density to be absorbed by the electronically delocalized structure of the DPA or for the DPA to transfer electron density to the AlH_3 -1451 if necessary. This will inhibit the excessive build-up of electron density at any one point in the AlH_3 -1451 crystal and, at the same time, the lack of symmetry of the electron distribution of the H-Al-H linkages on the surface will be less and the hydrogens will not be so far removed from their normal equilibrium positions.

5. New Stabilizers (U)

(U) A screening program of acetylenic derivatives and compounds containing one or more phenyl groups was re-initiated in anticipation of finding a compound which will be more effective than diphenylacetylene, and also possess a higher melting point and a lower vapor pressure.

(C) The compounds screened as possible stabilizers are listed in Table XII and their effect on AlH_3 -1451 decomposition curves is illustrated in Figures 22 and 23. Most of the compounds demonstrated a degree of activity; however, none exhibited the stabilizing effect or lengthening of the induction period comparable to that of DPA. Triphenylsilanol was also used as a stabilizing agent, but Talani results at 60°C . indicated it was less effective than DPA.

(U) Figure 23 illustrates the results obtained from an initial study of various acetylenic derivatives. All were similar in structure as they possessed a CH_2 group adjacent to the acetylenic bond; however, the compounds differed in the number of triple bonds available.

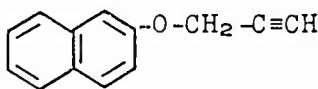
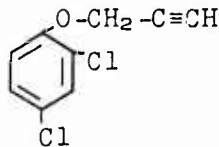

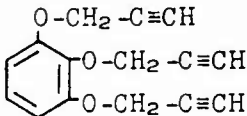
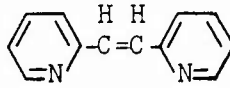
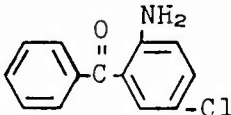
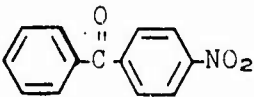
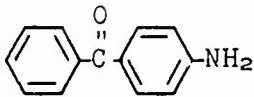
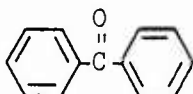
6. Aging Studies of Magnesium-Doped Aluminum Hydride-1451 (C)

(C) It was discovered from surveillance studies of neat aluminum hydride samples stored under an inert atmosphere, that large improvements in stability occurred with storage. This "aging" phenomenon was later found to be particularly characteristic of all magnesium-doped hydride. Because of the more than sevenfold improvement in thermal stability as a result of "aging", efforts were made to understand and characterize this phenomenon. It was expected that this would lead to further improvements in aluminum hydride stability.

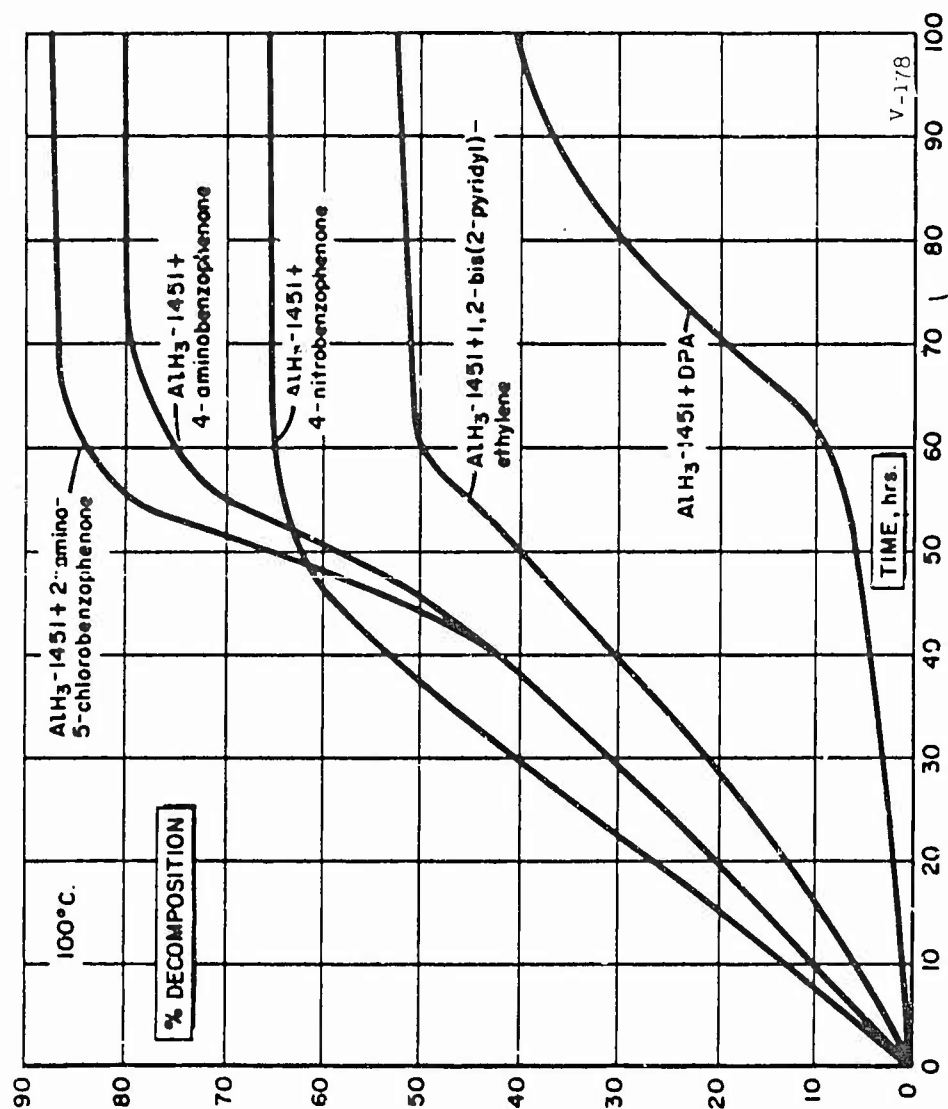
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Table XII

(C) New Compounds Screened as Potential Stabilizers
of Aluminum Hydride-1451

Name	Structure
2(2-Propynyloxy)naphthalene	
2,4-Dichlorophenylpropargyl ether	
p-bis(2-Propynyloxy)benzene	
1,2,3-tris(2-Propynyloxy)benzene	
1,2-bis(2-Pyridyl)ethylene	
2-Amino-5-chlorobenzophenone	
4-Nitrobenzophenone	
4-Aminobenzophenone	
Benzophenone	

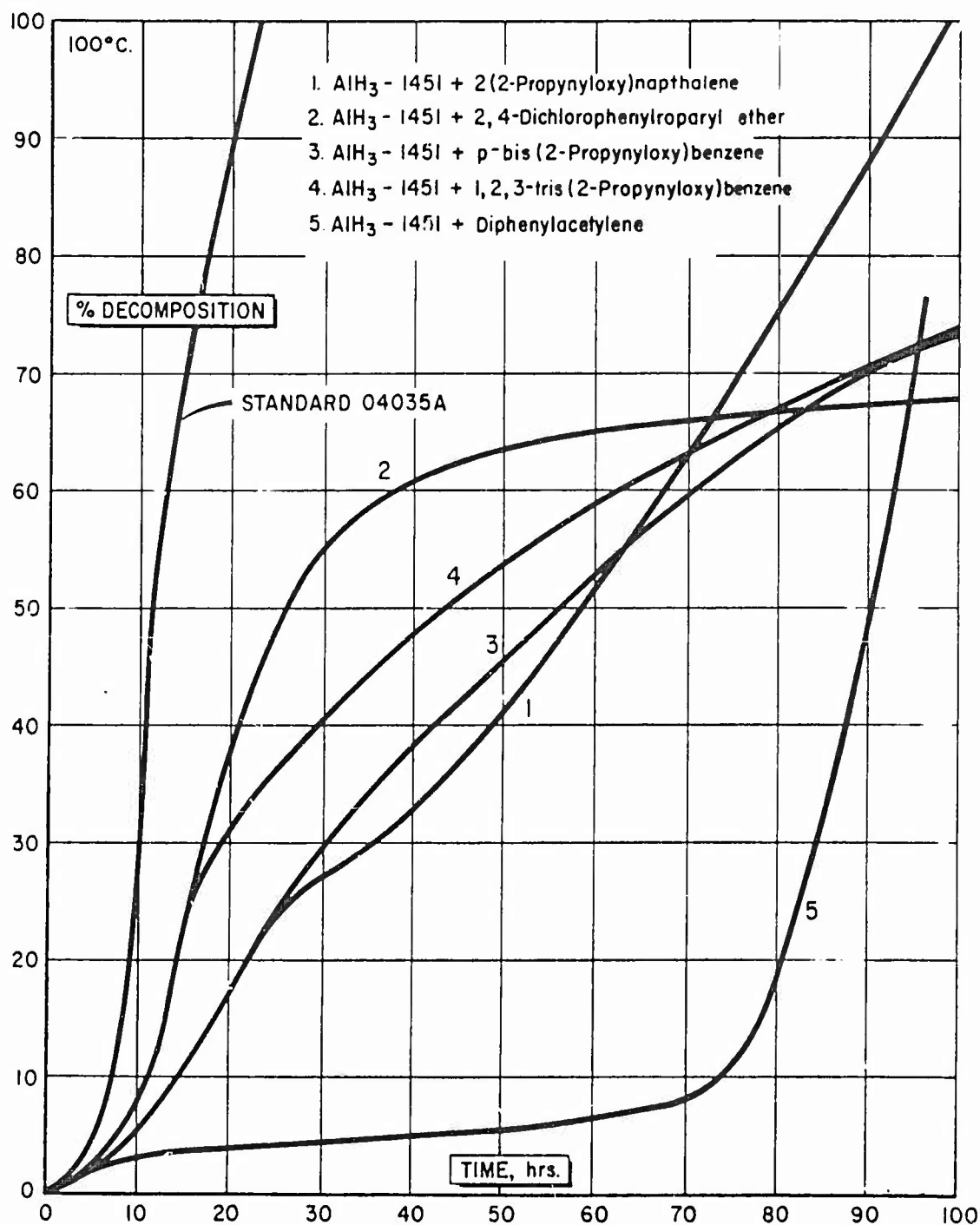
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(c) Fig. 22 - Evaluation of New Stabilizers for Aluminum Hydride-1451

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(C) Fig. 23 - Evaluation of Substituted Acetylenic Derivatives as Aluminum Hydride-1451 Stabilizers

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a. Effect of Storage Time at -15°C. (U)

(C) A number of magnesium-doped laboratory samples of AlH_3 -1451 which had been under surveillance at -15°C. for over a year showed significant improvement in thermal stability; the completed data are presented in Table XIII. Several lots required nearly 100 days before reaching 1% decomposition at 60°C., representing approximately a sevenfold improvement in stability. There is no indication that the samples attained their maximum stability; however, the degree of improvement for sample 5853-146 was much greater for the first 4-6 months than it was during the last six months. One sample, 8262-19, which had the best stability prior to storing, exhibited a phenomenal improvement, requiring approximately 170 days to reach 1% decomposition at 60°C. as shown in Figure 24. The results from this sample indicate that even better stabilities can probably be realized. Figure 25 summarizes the progressive improvement in thermal stability that has been achieved by a combination of magnesium incorporation, surface treatment with DPA, and "aging".

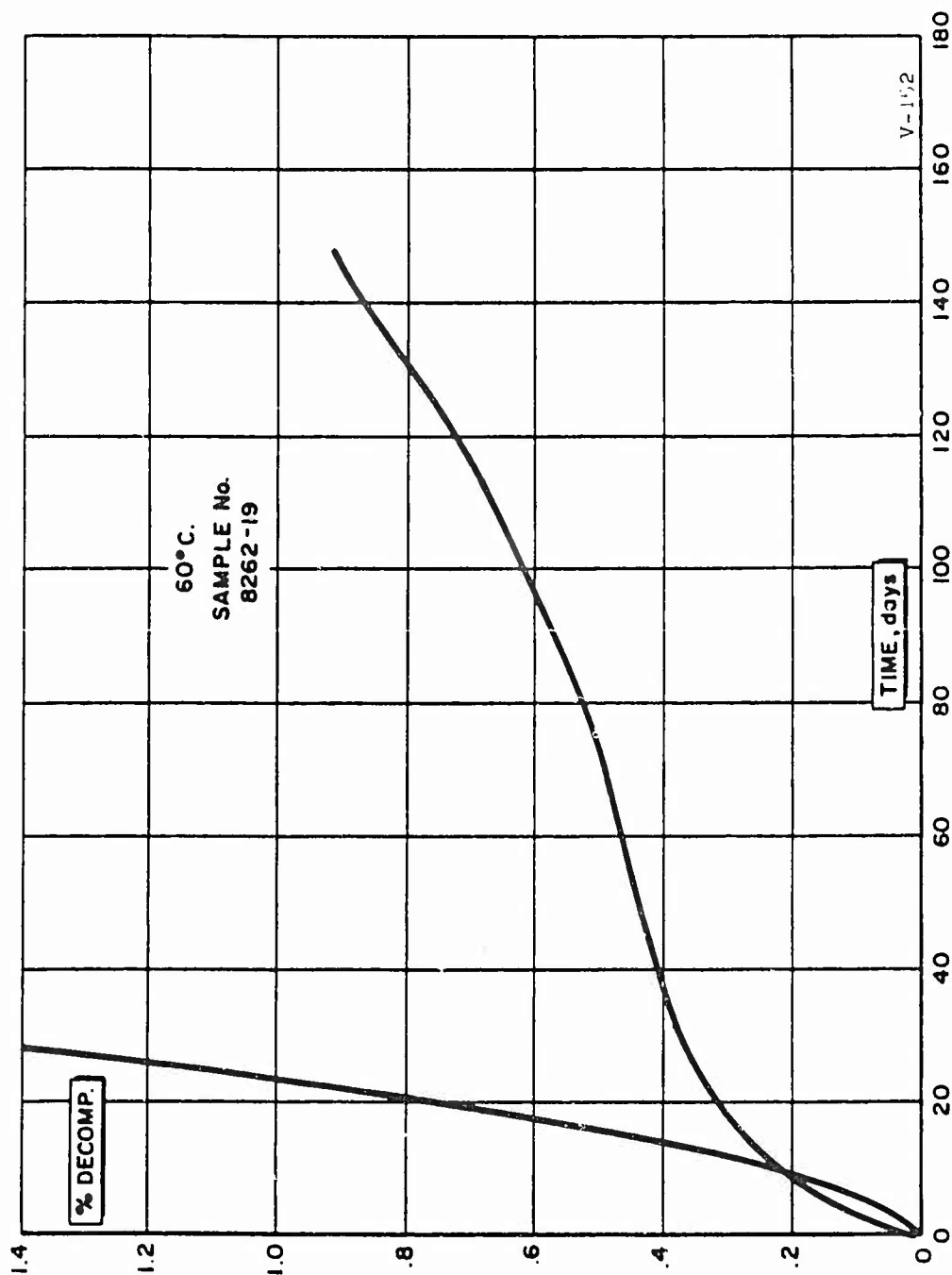
Table XIII

(C) Effect of Storage Time at -15°C. on Aluminum Hydride-1451

Sample Number	% Mg	Days to Reach 1% Decomposition at 60°C.			
		Original	4-6 Months	9-12 Months	18 Months
5853-131	1.64	13.5	22.5	27.0	--
5853-142	1.72	12.9	42.0	91.0	--
5853-141	1.53	6.8	26.0	46.0	--
5853-146	2.07	12.8	70.0	93.0	135.0
5853-150	2.3	14.5	29.5	107.0	128.0
8262-19	2.1	22.6	--	170	0.81 in 156 days
8262-48	1.0	14.0	--	82.0	0.88 in 156 days

(C) To further confirm the accuracy of the decomposition rates being measured from these "aged" samples, Sample No. 5853-150 was re-examined and its decomposition curve determined by a pressure transducer apparatus. A comparison between the decomposition rate measured by the standard Taliani apparatus versus the transducer apparatus is illustrated in Figure 26. The measured decomposition rates by the two different methods were essentially the same except for small differences during the early stages of decomposition. This information, obtained from duplicate samples which are known to be uncontaminated with mercury, is reassuring.

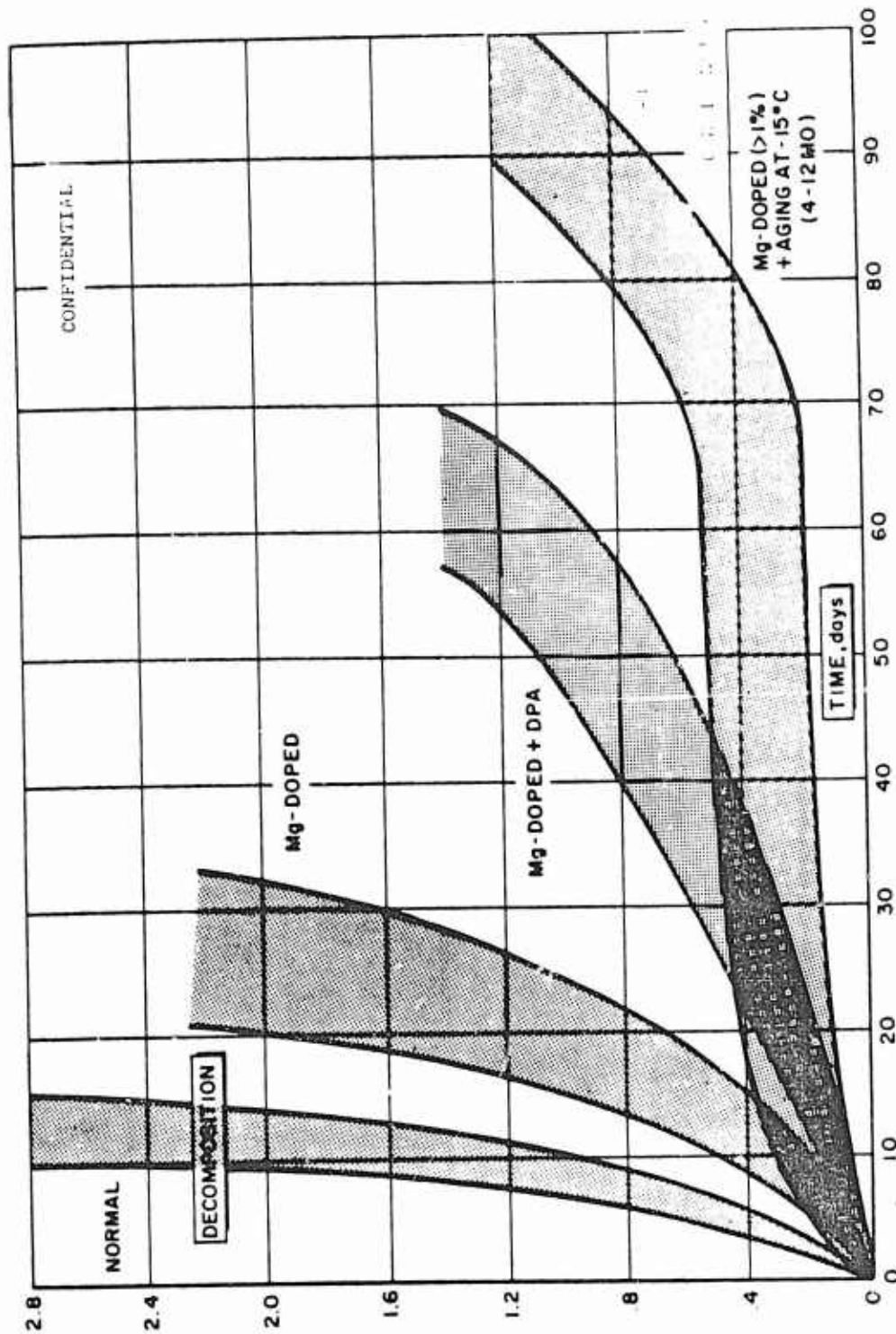
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(C) Fig. 24 - Effect of Storage Time at -15°C. on the Decomposition Rate of Magnesium-Doped Aluminum Hydride-1451

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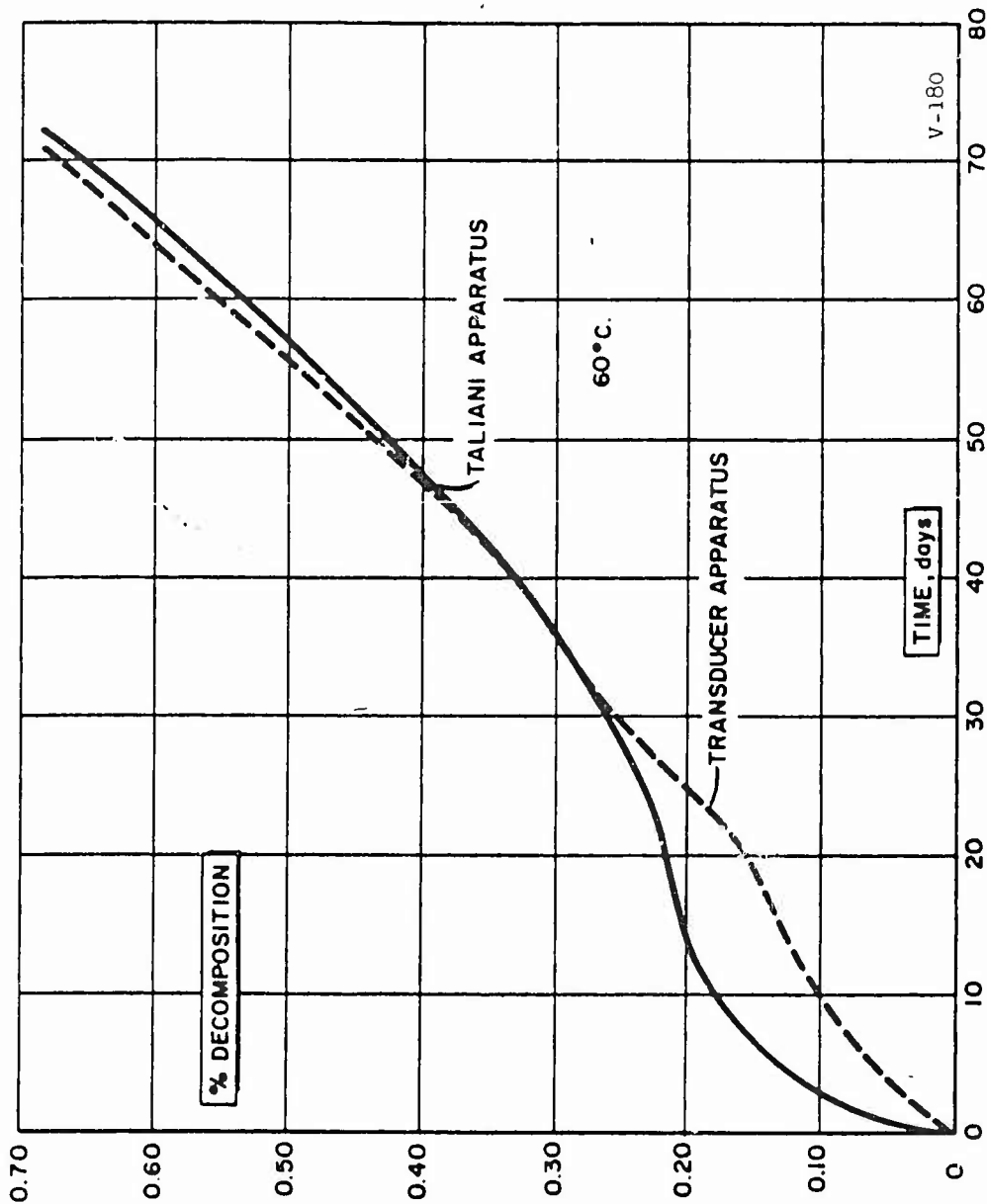


(U) Fig. 25 - Summary of Progress Achieved in Improving the Thermal Stability of Aluminum Hydride-1451

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(U) Fig. 26 - Comparison of the Decomposition Rate of an "Aged" Sample as Measured by a Taliani and Pressure Transducer Apparatus

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b. Effect of Magnesium Concentration on "Aging" (U)

(C) In an attempt to determine the effect of magnesium concentration in the hydride lattice on "aging", several older samples of hydride which had been stored for approximately 2 years at -15°C . were re-evaluated to determine their current stability. A summary of the results is shown in Table XIV.

Table XIV

(C) Effect of Magnesium Concentration on Stability of Aluminum Hydride-1451 Stored at -15°C .

Sample No.	% Mg	Days to Reach 1% Decomposition at 60°C .		Days Improvement
		Original	1-2 Years	
8262-89	0.3	8.5	10.5	2.0
8583-116	0.4	4.8	10.0	5.2
5853-81 ^a	0.6	3.0	9.5	6.5
5853-82	0.7	11.0	35.5	24.5
5853-83	0.8	13.5	26.0	12.5
5853-79	0.9	15.0	20.0	5.0
8262-48	1.0	14.0	82.0	68
5853-141 ^b	1.5	6.8	46.0	39.2
5853-131	1.6	13.5	27.0	13.5
5853-142	1.7	12.9	91	78.1
5853-146	2.1	12.8	93.0	80.2
8262-19	2.1	22.6	170	147
5853-150	2.3	14.5	107	92.5

^aVery poor bulk density.

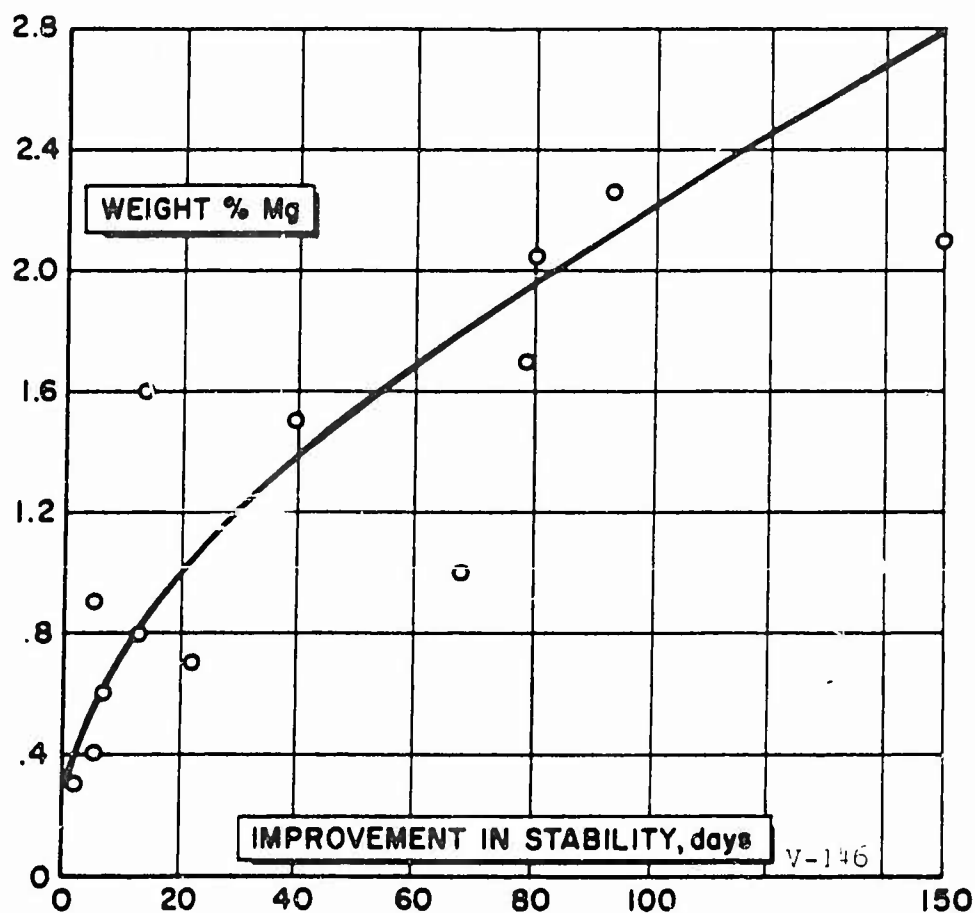
^bLess than 5% AlH_3 -1433.

(U) A plot of the percent magnesium versus the number of days improvement in stability as a result of "aging" is shown in Figure 27. The data show the hydride stability to increase as the magnesium concentration increases. As indicated by the apparent parabolic-shaped relationship, concentrations greater than 1.0% magnesium appear necessary for obtaining large improvements in stability.

c. Effect of "Aging" on Unit Cell Dimensions (U)

(C) It was pointed out by Dr. Eock of Edwards Air Force Base (9) that the incorporation of magnesium into the lattice of AlH_3 -

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(U) Fig. 27 - Improvement in Stability of "Aged" Samples
as a Function of Weight Percent Magnesium

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1451 resulted in an expanded unit cell but it was not known if "aging" also affected this property. In order to investigate this, the unit cell dimensions of three samples containing varying amounts of magnesium were compared before and after "aging". The unit cell dimensions of each sample were carefully determined from X-ray patterns taken on an AEG linear-type focusing camera with aluminum as a reference.

(U) The results, tabulated in Table XV, show that within experimental error the unit cell dimensions remained unchanged, and from this it must be concluded there is no correlation or relationship between improvement in stability as a result of "aging", and changes in the unit cell dimensions of the crystal lattice.

d. Initial Gassing of "Aged", Magnesium-Doped Aluminum Hydride-1451 (C)

(C) Another characteristic of "aged", magnesium-doped samples is a small amount of initial rapid gassing during testing at 60°C. This initial gassing on the Taliani was found to correlate roughly with the degree of improvement in thermal stability. The data therefore suggested that the gas, assumed at first to be hydrogen, was playing a very significant role in improving the thermal stability of aluminum hydride-1451.

(C) To further elucidate the effect of initial gassing, two samples which demonstrated a definite initial gassing and increased stability after a period of "aging" were degassed on a high vacuum line for approximately two weeks at ambient temperature. They were then removed and evaluated at 60°C. on a Taliani apparatus. It was extremely interesting to find both the initial gassing and "aged" stability exhibited by the samples had been removed by this treatment (Figures 28 and 29). The thermal stability of the hydride in the case of Sample 5853-83, was reduced completely to the rate it originally possessed immediately following preparation. Sample 5853-82 also lost most of its stabilization during degassing. These results suggested that the gas which was evolved was responsible for the increase in stability gained during storage and that it would be necessary to identify the evolved gas, and to determine, if possible, the mechanism responsible for the improvement in stability. Once a better understanding of this is obtained, it should lead to better control of the decomposition kinetics of aluminum hydride.

(U) The composition of the initial gas was quantitatively determined by mass spectrometry. The gas analysis from two "aged" AlH_3 -1451 samples is shown in Table XVI. Both samples were heated for a period of time before the evolved gas was released into the mass spectrometer.

(C) Analysis of sample 8262-103II after heating for 20 minutes at 80°C. showed 81% water and 15.7% hydrogen. The sample was then

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Table XV

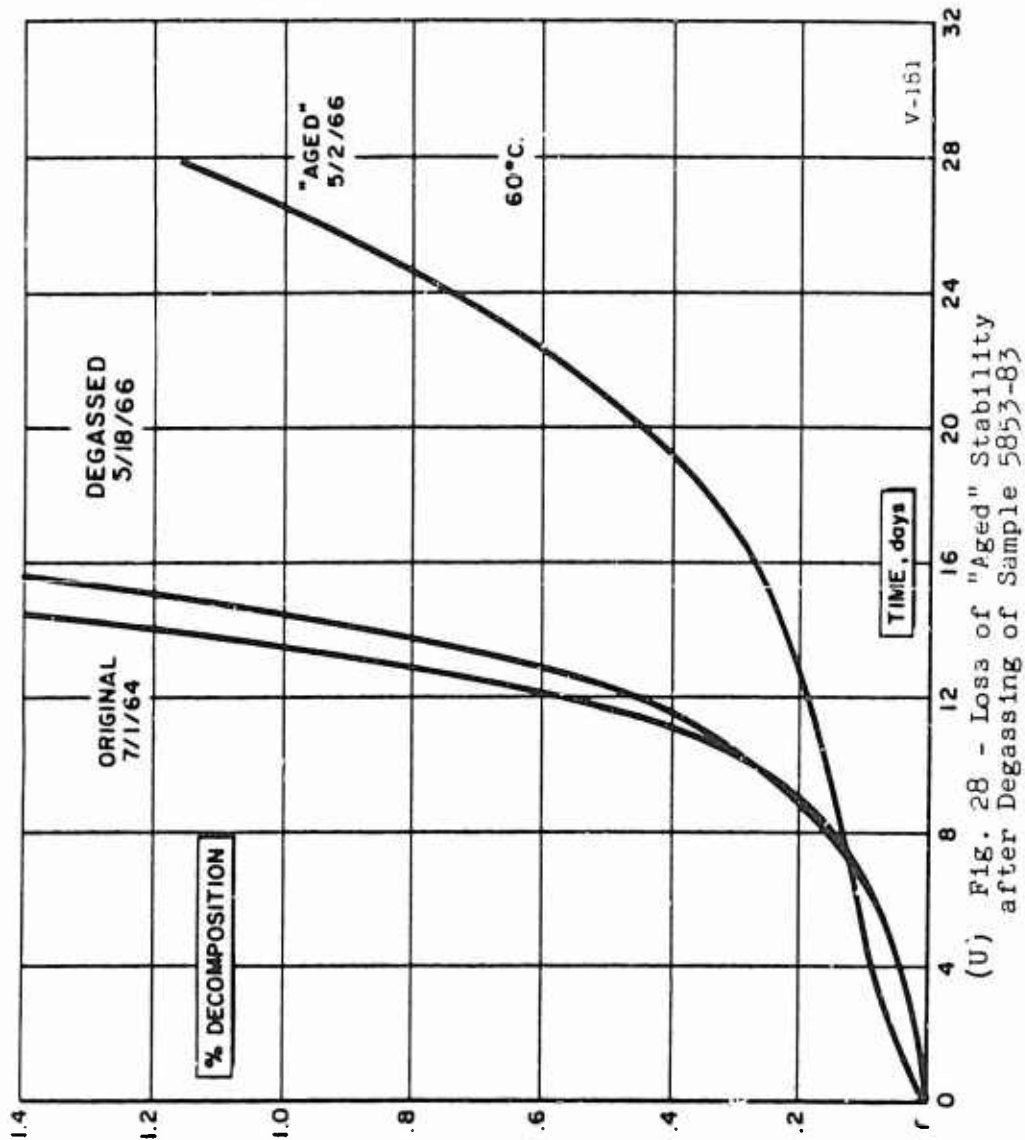
(c) Unit Cell Dimensions of Magnesium-Doped Aluminum Hydride-1451
Before and After Aging

Sample	% Mg	Unit Cell Dimensions, Å		
		Initial, January, 1965		After Storage for 20 Months at -15°C.
		a	c	
5853-23	0.6	4.4532 ± 0.0006	11.8246 ± 0.0005	4.4546 ± 0.0006 11.8285 ± 0.0010
5853-128	1.38	4.4589 ± 0.0006	11.8373 ± 0.0014	4.4577 ± 0.0006 11.8370 ± 0.0005
5853-145	2.09	4.4618 ± 0.0006	11.8426 ± 0.0005	4.4631 ± 0.0006 11.8431 ± 0.0030

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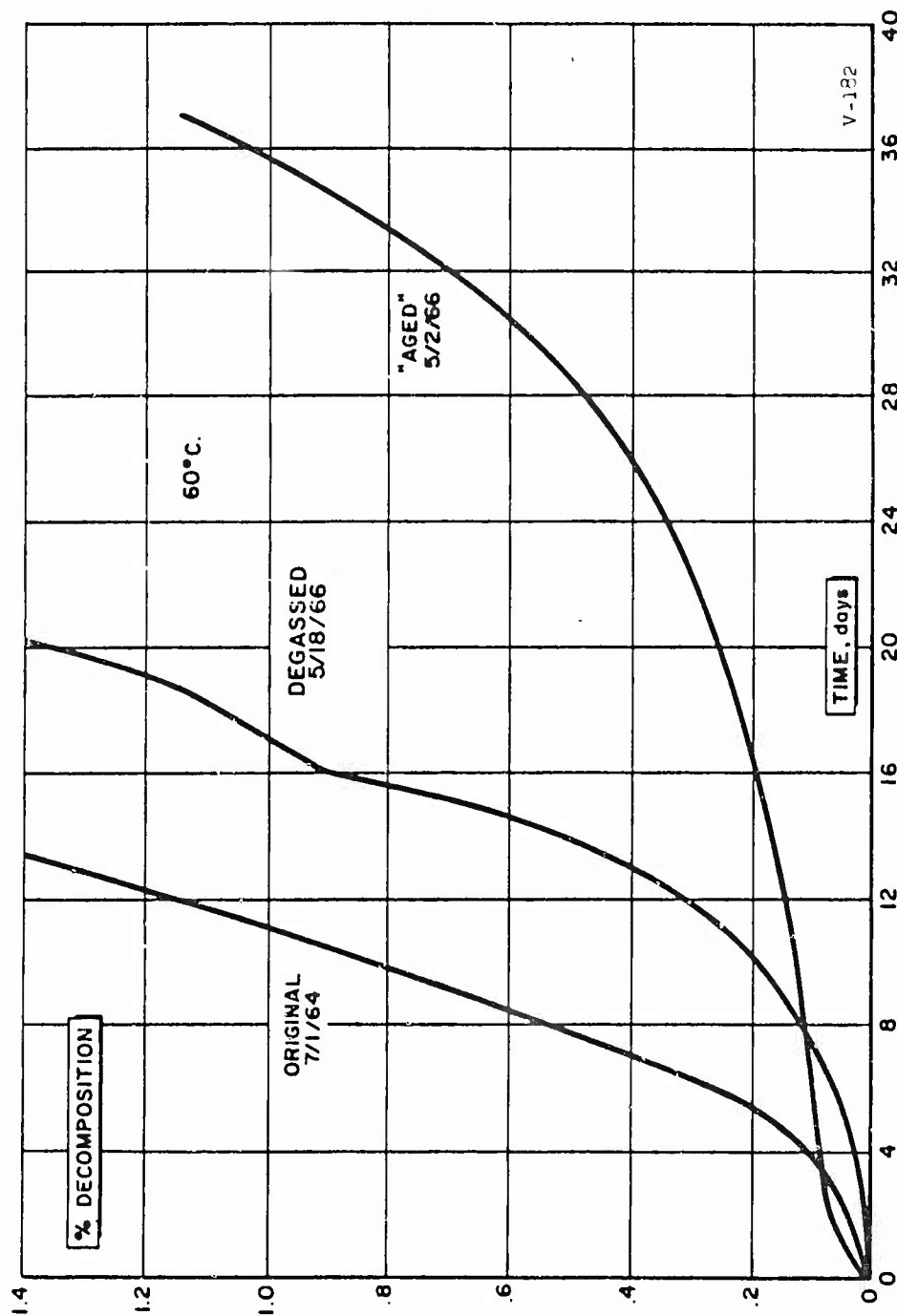
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(U) Fig. 29 - Loss of "Aged" Stability after Degassing of Sample 5853-82

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closed off from the mass spectrometer and again reheated for an additional 20 minutes at 80°C. Analysis of the gas this time indicated 88% water and 8.5% hydrogen. In addition to water and hydrogen, trace amounts of C_6H_6 , $(C_2H_5)_2O$, CO_2 , and N_2 or CO were also observed.

Table XVI

(U) Analysis of Initial Gas Evolved from "Aged" Hydride

<u>Sample Number</u>	<u>Gas Analysis, mole %^a</u>	
	<u>H₂O</u>	<u>H₂</u>
<u>8262-103II</u>		
a) 20 minutes at 80°C.	81	15.7
b) Additional 20 minutes at 80°C.	88	8.5
<u>5853-146</u>		
a) 20 minutes at 80°C. ^b	72.6	21.2
b) Additional 20 minutes at 80°C.	78.1	21.9

^aTrace amounts of C_6H_6 , $(C_2H_5)_2O$, N_2 or CO .

^bObserved 5.6 mole % CO_2 .

(U) Analysis of a second sample (5853-146) showed 5.6 mole % CO_2 in addition to large amounts of water and hydrogen as shown in Table XVII. It is interesting to note that this sample is extremely stable, requiring nearly 100 days to reach 1% decomposition at 60°C. The significance of the observed CO_2 is unknown but should be examined in future studies.

Table XVII

(U) Effect of Temperature on "Aging"^a

<u>Sample No.</u>	<u>Stability, days to 1% decomposition at 60°C.</u>			
	<u>Original</u>	<u>Ambient</u>	<u>-15°C.</u>	<u>Removed Ambient^b</u>
8262-103I	9.5	23.6	31	28
8262-103II	13.2	17.0	25.5	26

^aSamples stored ten months.

^bRemoved from -15°C. storage six months previous to above test.

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(U) It is now concluded that the initial gas from "aged" samples contains large amounts of water vapor which is playing a major role in the "aging" process.

(C) The "aging" phenomenon, however, is much more complex than simply treating the magnesium-doped material with moisture as might be inferred. Past techniques of surface treating magnesium-doped material with water after preparation have never produced a product with stability comparable to "aged" material. In addition, oxygen analyses of samples during storage at -15°C . and ambient temperature show approximately the same increase in oxygen concentration (Table XVIII), but the increase in thermal stability of the samples stored at -15°C . is much greater than those stored at ambient temperatures (Table XVII).

Table XVIII

(U) Oxygen Analysis of Stored Samples

Sample No.	Storage Temperature	Wt. % Oxygen	
		Original	After 1 yr. Storage
8262-103I ^a	-15°C .	$\sim 0.52\%$	1.10 ± 0.09
	Ambient		0.96 ± 0.09
8262-103II ^b	-15°C .	$\sim 0.3\%$	0.50 ± 0.06
	Ambient		0.46 ± 0.06

^aComposite of samples prepared in an atmosphere of 10,000 ppm O_2 .

^bComposite of samples prepared under anhydrous conditions.

(C) On the basis of these observations it must be concluded that specific conditions are necessary if maximum benefit is to result from water treatment of the hydride. These conditions must depend on the type of surface structure formed as a result of water in combination with magnesium-doped AlH_3 -1451, and must also be greatly influenced by process parameters.

e. Kinetic Studies of "Aged," Magnesium-Doped Aluminum Hydride-1451

(C) The activation energy for the acceleration period during the decomposition of normal AlH_3 -1451 is approximately 23.0 ± 1.5 kcal./mole as determined by the Prout-Tompkins equation given below.

$$\ln \frac{P}{P_f - P} = kt$$

(C) It has been previously reported that the activation energy of magnesium-doped hydride varies widely during the acceleration

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period (1). Preliminary data from only two magnesium-doped samples are summarized in Table XIX. The activation energy for the acceleration period of the magnesium-doped samples is apparently changing with time. The samples originally had an activation energy of 27.0 and 28.6 kcal./mole; however, after five and seven months' storage, the activation energy had changed to approximately 30.7 kcal./mole. Taking the average of the four values after storage (30.7 kcal./mole) and comparing it to the average of the two samples originally, (27.8 kcal./mole) a change of 2.9 kcal./mole is measured. There appear to be no significant effects resulting from differences in storage temperature.

Table XIX

(U) Effect of Time and Temperature
on Activation Energy of Acceleration Period

Sample No.	Activation Energy, kcal./mole		
	Original	Storage Temperature ^a	
		Ambient	-15°C.
8262-103II	27.0	32.1	29.9
8262-103I	28.6	30.1	30.8

^aSample 8262-103II stored five months;
8262-103I stored seven months.

f. The Effect of Ambient Storage on "Aged" Samples (U)

(C) A sample exhibiting an increase in thermal stability with age at -15°C. was removed from cold storage and allowed to stand at ambient temperature. The decomposition rate of the sample was measured immediately after removal from storage and subsequently every 24 hours for 4 days. The data shown in Table XX indicate during the four days' storage at ambient temperature. The days required to reach 1% decomposition decreased from an estimated 28 to 18.9 and the initial gassing from 0.19% to 0.048% decomposition after two days.

(C) A decrease in initial gassing with increasing storage time at ambient temperature suggests the loss of adsorbed water as discussed in Section B.5.d. In this case, however, the loss of water is probably not a result of dehydration but due to diffusion inward through the oxide/oxyhydroxide surface where it reacts with aluminum hydride.

(C) Apparently it is possible to condense water on the surface of the hydride at -15°C. without a reaction. Removal from storage at -15°C. allows the moisture present to react with the hydride causing a decrease in the initial gas and stability observed at 60°C.

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Table XX

(U) Effect of Pretreating "Aged" Sample 8262-103II

<u>Storage Time at Ambient Temp., days</u>	<u>Initial Gassing, % Decomposition after 2 days at 60°C.</u>	<u>Stability, days to reach 1% decomposi- tion at 60°C.</u>
0	0.19	28 est.
1	0.16	27
2	0.092	23.8
3	0.071	21.7
4	0.048	18.9
7 (constant pumping under vacuum)	0.034	17
7 (static vacuum)	0.064	21

(C) These results are puzzling when compared to the stability obtained from the same sample after six months' storage at ambient temperature following removal from cold storage. The data in Table XVII show that the sample previously stored at -15°C. retained its increased stability after storage at ambient temperature. This appears to be in contradiction with the above data which show a considerable loss in stability after storage for four days at ambient temperature.

(C) Table XX also summarizes experiments which further evaluate the original "pumping" experiment. Very little difference was observed in the stability and initial gassing of the sample stored for 4 days at ambient temperature compared to the same sample stored 7 days under constant pumping. Hence, it appears storage time and temperature, but not vacuum, are the important factors. Some difference was noted on storage for 7 days under constant pumping compared to static vacuum conditions (17 days vs. 21 days to reach 1% decomposition).

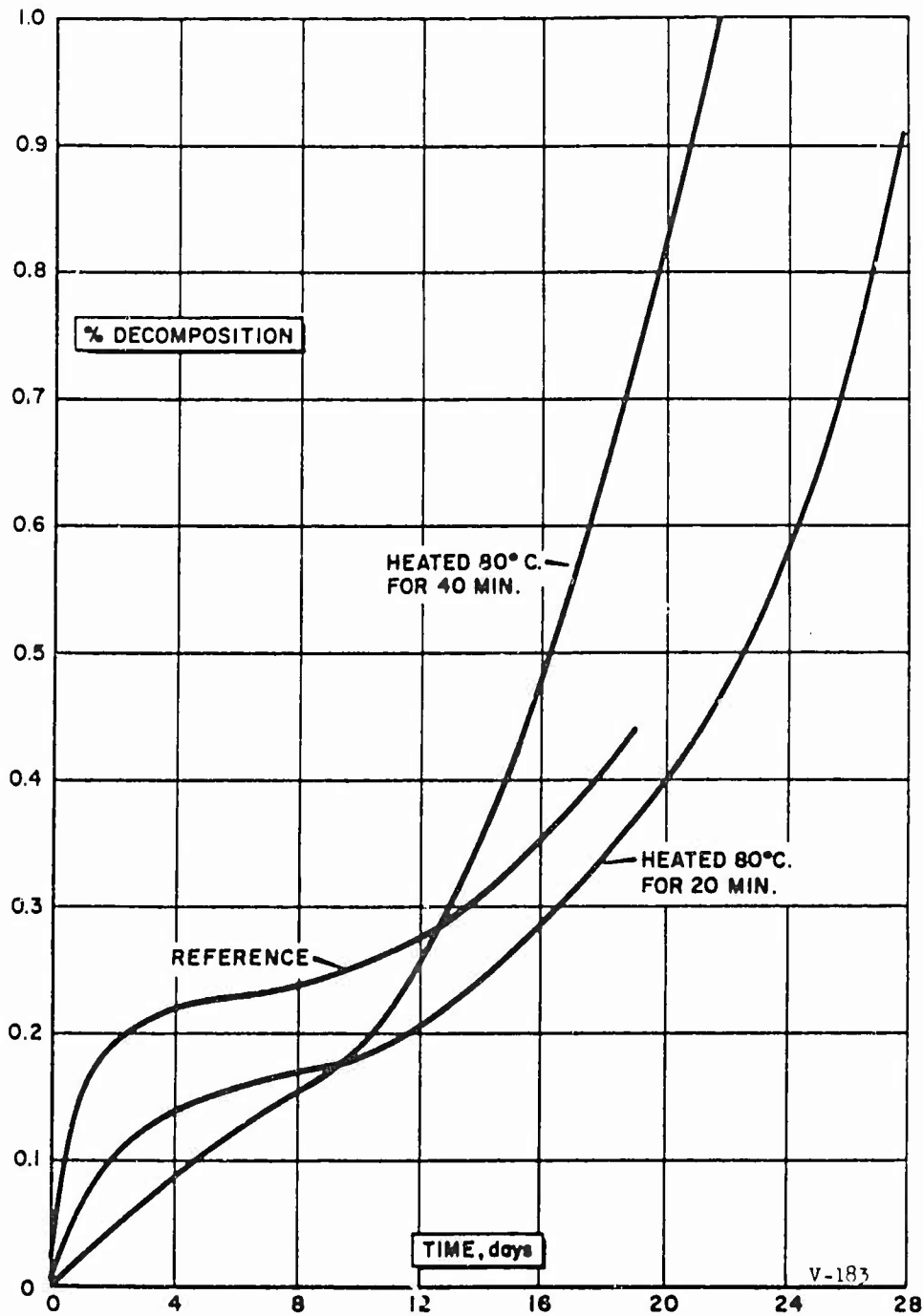
g. Heat Treatment of Magnesium-Doped Aluminum Hydride-1451 (C)

(C) Techniques for accelerating the "aging" of magnesium-doped AlH_3 -1451 were investigated. Previous results suggested that the sample upon removal from cold storage was undergoing a heat treatment when placed in the Taliani apparatus at 60°C. for evaluation, and that this was responsible for its increased stability.

(C) Preliminary data obtained from heat treating a sample at 80°C. for a short period of time before evaluation at 60°C., as shown in Figure 30, demonstrated only a small amount of improvement in stability. However, a 20 minute heat treatment at 80°C.

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(U) Fig. 30 - Effect of Heat Treating "Aged" Samples

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did reduce the initial gassing. Based on the premise that the "aging" phenomenon may involve the freezing of moisture on the surface of the hydride followed by heat-treating at 60°C. during evaluation, an attempt was made to duplicate this process.

(C) Magnesium-doped AlH_3 -1451 was placed in an appropriate apparatus and an amount of moisture equivalent to 1% hydrolysis was frozen on the surface of the hydride at -196°C. Samples were then allowed to warm up to room temperature for twenty-four hours before heat-treating at 80°, 70°, 60°, 50°, and 40°C. After this moisture and heat treatment step, they were evaluated on the Taliani apparatus at 60°C.

(C) This technique "essentially" reproduces the "aging" phenomenon and in a matter of hours stabilizes the hydride to the same degree as previously attained by four to six months' storage at -15°C. It is interesting to note from the results shown in Figure 31 that the samples heat-treated at 80°, 70°, and 60°C. exhibited no initial gassing whereas those heat-treated at 50°C. and 40°C. did; a direct correlation between the amount of initial gassing and stability was again observed. The sample, moisture- and heat-treated at 40°C., exhibited the greatest initial gassing (0.3%) and stability (47 days to 1% decomposition) compared to the reference sample (21 days to 1% decomposition).

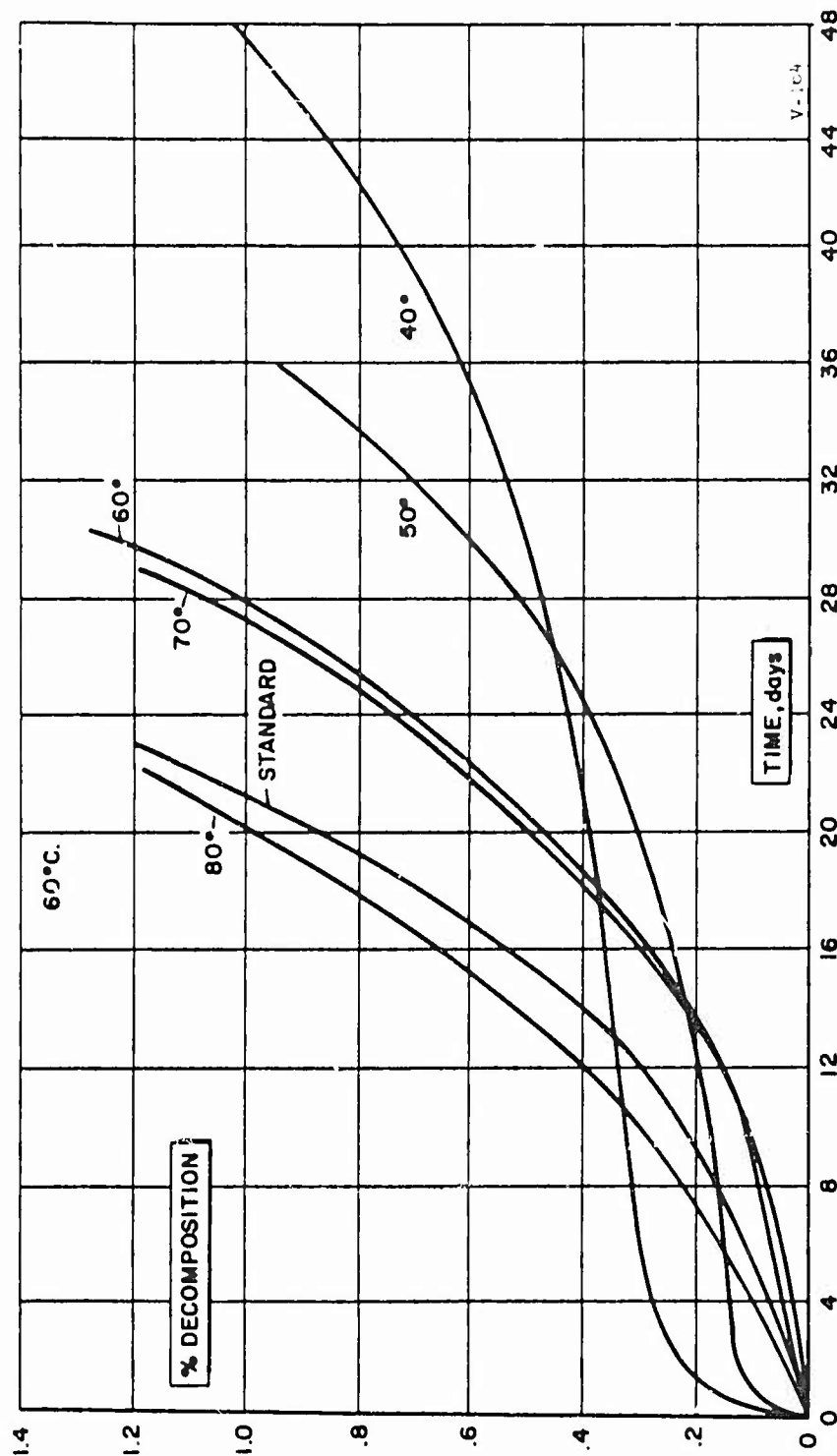
(C) It was surprising to find less than 10% (including the initial gassing at 60°C.) of the gas expected from 1% hydrolysis was evolved. This suggests that water is held by the oxide film formed on the hydride surface, preventing it from coming in contact with the hydride.

(U) Higher temperature and lower heat-treating time, as shown in Figure 32, did not prove to be successful. Samples were heated at 100°, 90°, and 80°C. for 3, 4, and 5 hours, respectively. No large change in stability was observed.

7. Storage under Hydrogen Pressure (U)

(C) Various types of AlH_3 -1451 were stored under a hydrogen pressure of 7500 psi. for a total of 5 months at ambient temperature to determine if an increase in thermal stability could be achieved by annealing under these conditions. The samples were evaluated after 2 to 5 months' storage. The data are summarized in Table XXI for (i) macrocrystalline, (ii) magnesium-doped, DPA-treated, and (iii) magnesium-doped AlH_3 -1451. Little, if any, change was observed in the thermal stability of macrocrystalline and magnesium-doped AlH_3 -1451. However, magnesium-doped, DPA-treated AlH_3 -1451 appeared to have increased in thermal stability in 2 months from 19 to 32 days and in 5 months from 19 to 22.5 days before reaching 1% decomposition at 60°C. Because additional storage produced a decrease in stability of the DPA-treated material, this does not appear to be a useful technique for improving the thermal stability of AlH_3 -1451.

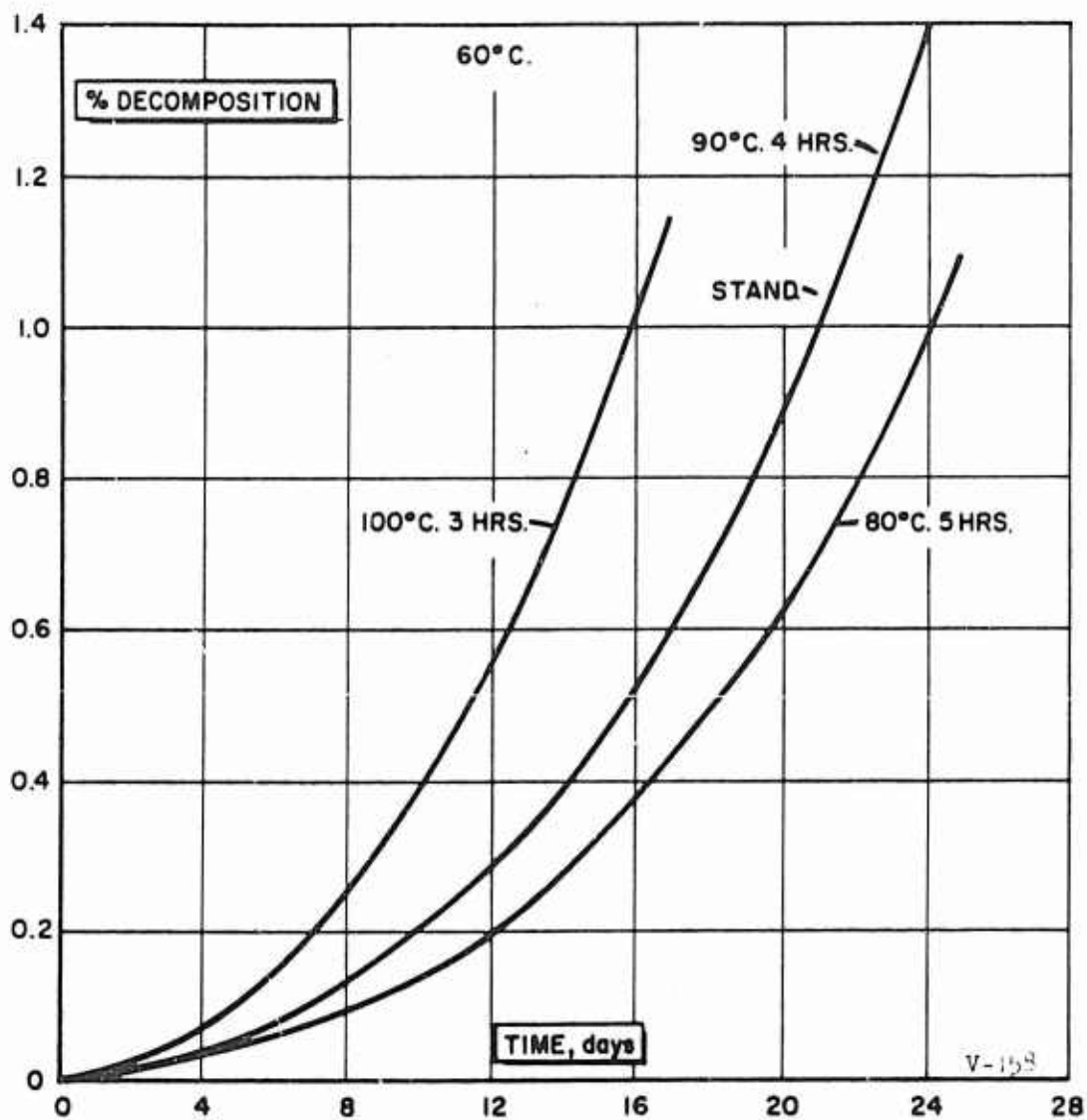
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(C) Fig. 31 - Effect of Moisture and Heat Treatment
at Low Temperatures on Aluminum Hydride-1451 Stability

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(C) Fig. 32 - Effect of Moisture and Heat Treatment at High Temperatures on Aluminum Hydride-1451 Stability

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Table XXI

(U) Effect of Storage under Hydrogen Pressure
on the Stability of Various Types of Hydride

<u>Hydride Type</u>	<u>Stability, days to 1% decomposition at 60°C.</u>		
	<u>Original Sample</u>	<u>Sample stored at 7500 psi H₂ 2 Months</u>	<u>5 Months</u>
Macrocrystalline	7.9	7.2	7.1
Magnesium-doped	12.4	12.5	12.5
Magnesium-doped, DPA-treated	19.0	32.5	22.5

8. Cycling Decomposition Temperature (U)

(C) The decomposition rate of AlH₃-1451 has usually been measured under isothermal conditions. However, in propellant applications the temperature of the hydride may be subjected to a variation in temperature depending upon the storage conditions. Therefore, it was believed desirable to examine the decomposition rate obtained by cycling the temperature and compare it to the isothermal decomposition rates.

(U) The temperature was cycled every twelve hours between 70°C. and 90°C. The same sample was then decomposed at 90°, 80°, and 70°C. under isothermal conditions for comparison purposes. The resulting decomposition curves are shown in Figure 33. It was thought that cycling the temperature between 70°C. and 90°C. would be very similar to the decomposition rate one would achieve at 80°C. which is the average of the two temperatures.

(U) The cyclic decomposition curve between 70°C. and 90°C. does roughly approximate the isothermal decomposition curve at 80°C. At these elevated temperatures the length of the induction period is very sensitive to change in temperature. Hence, the starting temperature is very important in obtaining this type of correlation. It is expected that the starting temperature would be less critical at lower temperatures.

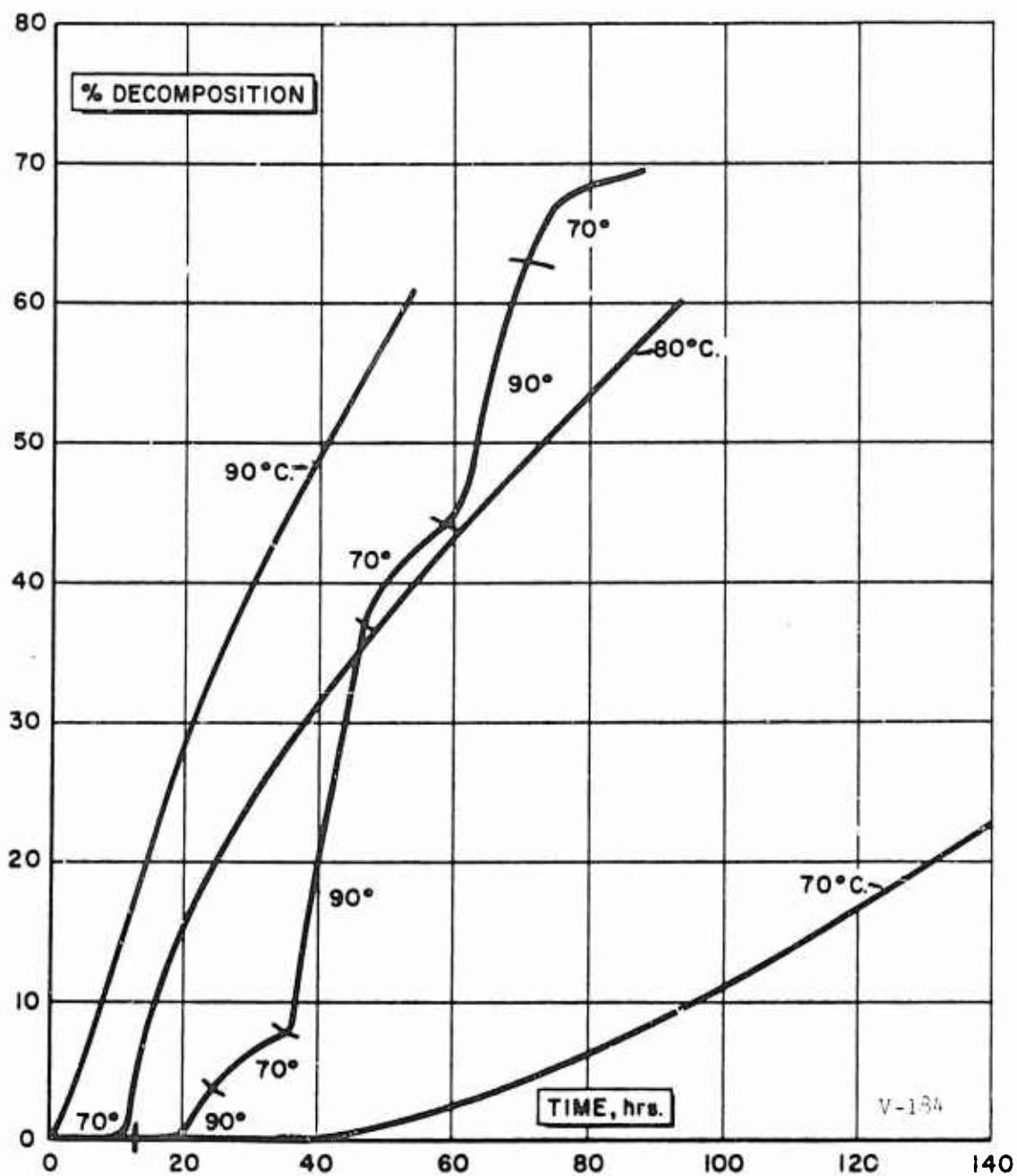
C. CRYSTAL STRUCTURE STUDIES OF ALUMINUM HYDRIDE-1451 (U)

(U) Diagrams depicting the unrefined structure of aluminum deuteride have been previously discussed and shown (1). Additional refinement of the aluminum deuteride-1451 structure has been achieved during the past quarter.

(U) The aluminum deuteride structure has three unknowns: a position parameter, a temperature parameter for D, and a temperature

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(C) Fig. 33 - Effect of Cyclic Temperature on Decomposition Rate of Aluminum Hydride-1451

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parameter for Al. Estimated values of 2.0 for the Al temperature factor and 4.0 for the D temperature factor were used during the refinement of the D position parameter. Neutron structure factor calculations for values of $X = 0.640$ (0.005) 0.690 were done for a subset of 19 reflections of the total indexed set of 60. The agreement factors continue to improve as X is decreased as shown in Table XXII.

Table XXII

(U) Neutron Structure Factor Calculations $R_1 = \Sigma/\Delta I / \Sigma/I_{\text{obs}}$

<u>X</u>	<u>R₁</u>	<u>X</u>	<u>R₁</u>
0.640	0.2925	0.670	0.3677
0.645	0.2937	0.675	0.3842
0.650	0.2966	0.680	0.3999
0.655	0.3175	0.685	0.4151
0.660	0.3369	0.690	0.4310
0.665	0.3507		

(U) A comparison of the calculated and observed intensities indicates that the estimated temperature factors may be too high. Values of 1.0 for Al and 2.0 for D are currently being used for calculation with $X = 0.625$ (0.005) 0.645.

(U) The Al-D distance in this structure is, at the present state of refinement, 1.704 Å. The refinement has shown that the column of hydrogen atoms parallel with the Z-axis is not collinear along the Z-axis but is displaced to the right or left by a finite value. This refinement of the structure is shown in projection on the (001) plane in Figure 34.

D. LONG-TERM SURVEILLANCE OF NEAT ALUMINUM HYDRIDE-1451 (C)

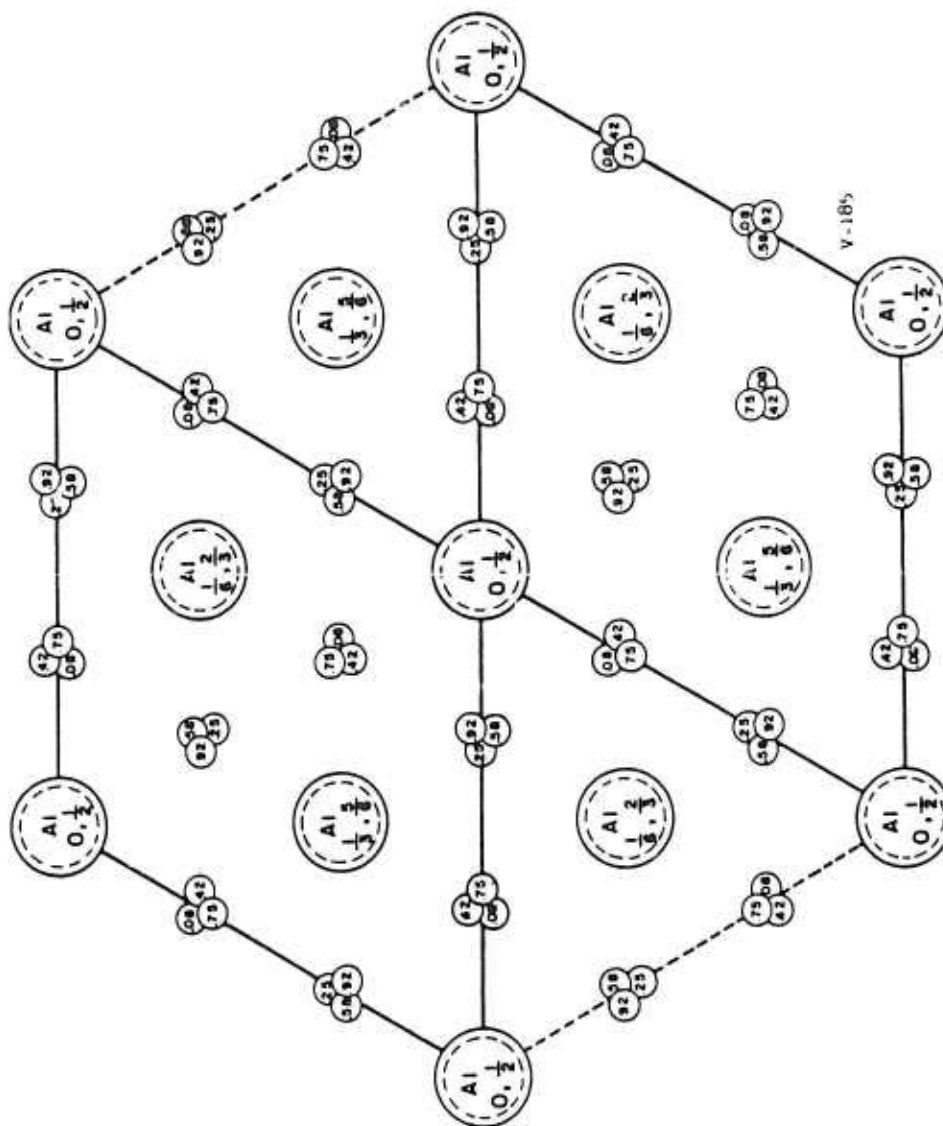
(C) Many samples of aluminum hydride have been stored neat and in propellant formulations at 40°C., ambient temperature, and -15°C. to determine the actual shelf life of aluminum hydride at these temperatures. The object of this study is to check the accuracy of the predicted shelf life and to verify that the improvements made in the thermal stability of aluminum hydride as determined by accelerated testing at 60°C. are also realized at the lower temperatures. Surveillance of aluminum hydride propellant represents the "acid test" since it evaluates both long-term stability and compatibility of the hydride with commercial propellant ingredients.

(C) A number of macrocrystalline aluminum hydride samples have been stored in taped glass vials under an inert atmosphere at ambient

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(U) Fig. 34 - Schematic Drawing of the Structure of Aluminum Deuteride-1451 in Projection on the (001) Plane

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temperature at -15°C . for more than two years. Samples at 40°C . have been stored for over 200 days and are exposed to light.

1. Storage at 40°C . (U)

(C) A summary of the decomposition rates measured from a series of neat, normal macrocrystalline samples stored at 40°C . is given in Table XXIII. The average percent decomposition for the six macrocrystalline lots is plotted in Figure 35 versus storage time in days. A plot of the decomposition rates measured for these samples over a period of 222 days yielded a typical decomposition curve for aluminum hydride. After 100 days at 40°C ., approximately 2% decomposition was observed; after 222 days, 36.6% decomposition was measured. Therefore, it can be concluded that a significant amount of decomposition would occur for normal macrocrystalline hydride if stored at 40°C . for periods of time much greater than 3 months.

Table XXIII

(C) Long-Term Storage Stability of Aluminum Hydride-1451 at 40°C .

Sample Number ^a	Decomposition ^b , %			
	Storage Time, days			
	80	97	202	222
04185A	1.3	1.3	23.0	42.4
04195	1.8	2.4	16.9	35.0
04265B	1.1	2.2	16.7	33.3
06255	0.2	1.7	14.3	35.0
06275	1.2	2.5	20.4	38.0
06285	1.0	2.2	15.9	36.2
Average % Decomp.	1.1	2.1	17.9	36.6

^aSamples stored 3 months in cold storage prior to evaluation.

^bDetermined by carbon and hydrogen analysis; hydrogen $\pm 1\%$ of total.

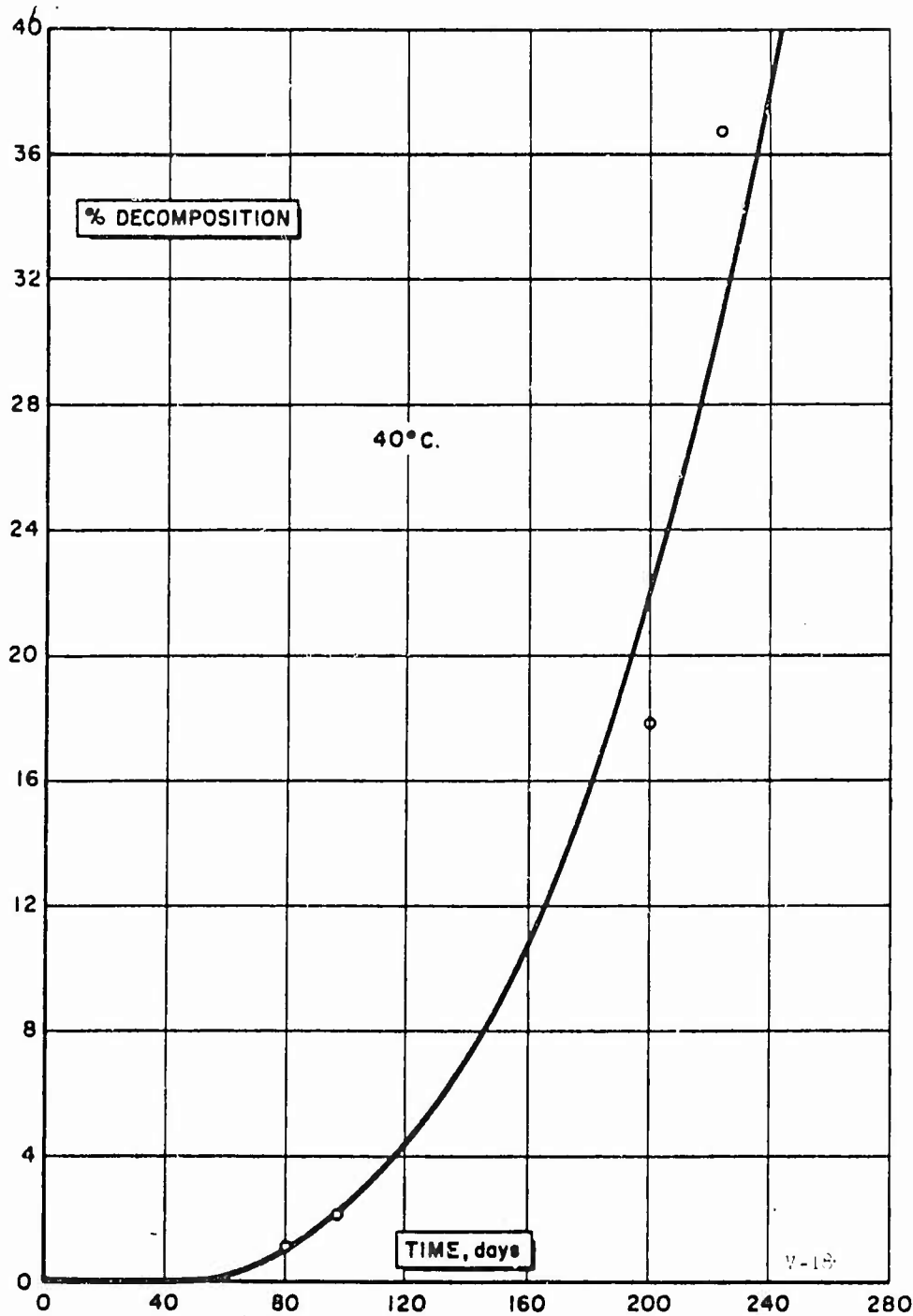
(C) The effect of storage at 40°C . on the thermal stability of aluminum hydride, as determined by the Taliani test at 60°C ., for the same six lots of macrocrystalline hydride is presented in Table XXIV.

(C) Eight pilot plant lots of magnesium-doped AlH_3 -1451 are also being stored at 40°C . The effect of storage on the thermal stability of the samples is summarized in Table XXV. The samples containing 0.48% to 1.35% magnesium exhibited a stability of 12.0 to 25.5 days before reaching 1% decomposition at 60°C . The results

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(U) Fig. 35 - Average Decomposition Curve
for Macrocrystalline Aluminum Hydride-1451 at 40°C.

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obtained at 40°C. for the two types of hydride are compared in Figure 36. The original data previously reported for the first four lots of hydride shown in Table XXV were in error due to a faulty temperature controller and thermometer. The new data for these lots shown in Figure 36 and Table XXV therefore differ from those previously reported.

Table XXIV

(C) Effect of Storing Aluminum Hydride-1451 at 40°C. on Thermal Stability

Sample Number	Days to Reach 1% Decomposition at 60°C. ^a				
	Storage Time, days				
	Original	16	42	63	96
04185A	6.6	4.9	2.6	3.5	1.25
04195	6.6	4.8	4.5	3.4	1.1
04265B	7.5	5.8	4.7	3.1	1.1
06225	8.7	8.0	6.2	3.6	2.4
06275	6.2	5.6	4.6	3.9	0.9
06285	6.6	5.9	3.8	2.5	1.4
Average Stability	7.0	5.8	4.4	3.3	1.4

^aTaliani test $\pm 0.2\%$ decomposition.

Table XXV

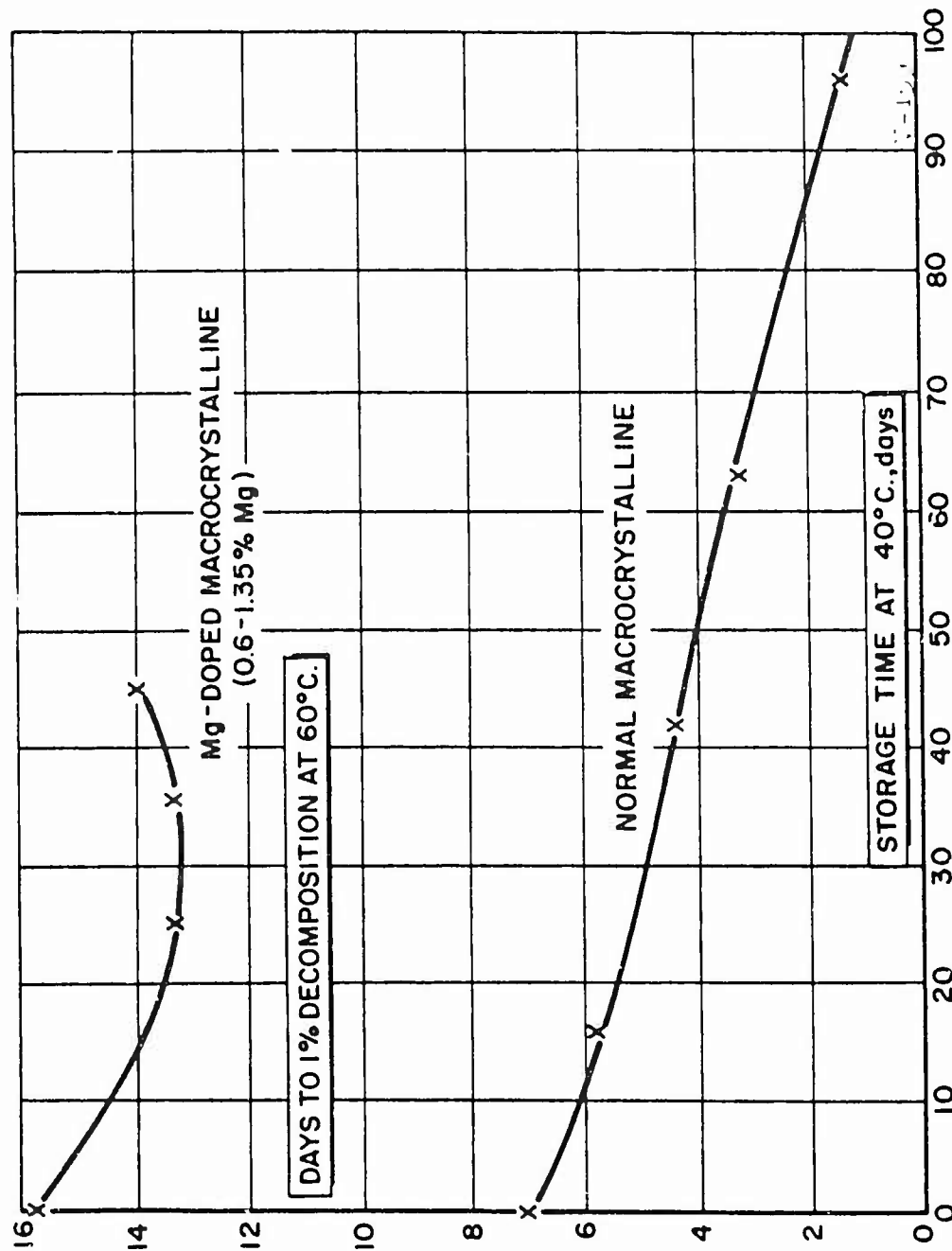
(C) Effect of Storing Magnesium-Doped Aluminum Hydride-1451 at 40°C.^a on Thermal Stability

Sample Number	% Mg	Days to Reach 1% Decomposition at 60°C. ^b					
		Storage Time, days					
		Original	7	21	35	42	49
01206	0.6	13.3	13.2	12.8	13.5	11.4	12.2
01216	0.67	14.5	13.6	13.5	13.0	11.2	11.4
01286	0.48	13.2	12.2	12.8	11.5	11.4	9.8
01316	0.81	12.0	11.6	10.4	10.8	11.1	9.5
06206	1.26	11.7	10.1	8.9	9.2	8.8	8.1
06276	1.35	25.5	--	18.8	20.0	24.1	23.5
06286	0.90	19.0	17.3	16.9	16.8	18.2	18.0
06386	0.86	16.8	12.9	12.6	12.4	13.1	14.8
Average		15.8	13.0	13.3	13.4	14.0	13.8

^aLots also placed under surveillance at ambient temperature and -15°C.

^bTaliani test $\pm 0.2\%$ decomposition.

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(c) Fig. 56 - Comparison of the Effect of Storage at 40°C. on the Thermal Stability of Normal and Magnesium-Doped Macrocrystalline Aluminum Hydride-1451

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(C) It was found for each of the six lots of normal macrocrystalline hydride stored at 40°C. the stability consistently decreased during a storage period of 96 days. The average stability of the magnesium-doped samples also decreases as storage time increases, although the curve appears to reach a plateau within 42 days. It is interesting to note the samples change color from white to gray after only approximately 4 days storage at 40°C. In contrast to normal macrocrystalline hydride, the improved stability exhibited originally by the magnesium-doped samples is essentially maintained over this period of time. The latest data suggest the magnesium-doped samples may be undergoing an accelerated "aging" phenomenon.

2. Storage at Ambient Temperature and -15°C. (U)

(C) The hydrogen analyses obtained for eleven different lots of normal macrocrystalline Dow Pilot Plant hydride stored for various periods of time at ambient temperature and -15°C. are summarized in Table XXVI. Samples 06104AT and 07084T are the same as 06104A and 07084, respectively, except that they have been treated with acrylonitrile (VCN) and sample 3655-85 is a laboratory composite. These samples have been stored for a period of 1.8 to 2.3 years. The percent decomposition is determined by the change in hydrogen content. Elemental analysis has shown that the hydrogen value obtained after this period of time is still within the experimental error of the method, accurate to $\pm 1\%$ decomposition of the measured value. Examination of the samples shows that those stored at ambient temperature have turned light gray, indicating a small amount of decomposition, whereas those stored at -15°C. are still white. Using these data, the hydrogen values were plotted as a function of storage time and a line drawn through the points with the origin represented by the average hydrogen value obtained from the sample stored at -15°C. Using this technique to evaluate the data, Table XXVII summarizes the percent decomposition as a function of time and temperature for each of the samples. It is obvious from the measured hydrogen values and the color of the samples stored at -15°C. that no decomposition has occurred over a period of approximately two years. The samples stored at ambient temperature appear to have decomposed less than 1% during this same period, although these numbers are not absolute values but represent only an indication of the amount of decomposition.

(C) The effect of temperature on the rate of decomposition of aluminum hydride is illustrated in Figure 37. This relationship is derived from the time it takes a sample to reach 1% decomposition and is shown for normal macrocrystalline hydride and macrocrystalline hydride containing 1.9% magnesium as a crystal lattice stabilizer. Originally, a comparison of the time it takes to reach $\pm 1\%$ decomposition at 60°C. and above resulted in two parallel lines which were extrapolated from the last experimentally determined point at 60°C. to 25°C. (broken line). This indicated that 1% decomposition should be observed from the normal macrocrystalline

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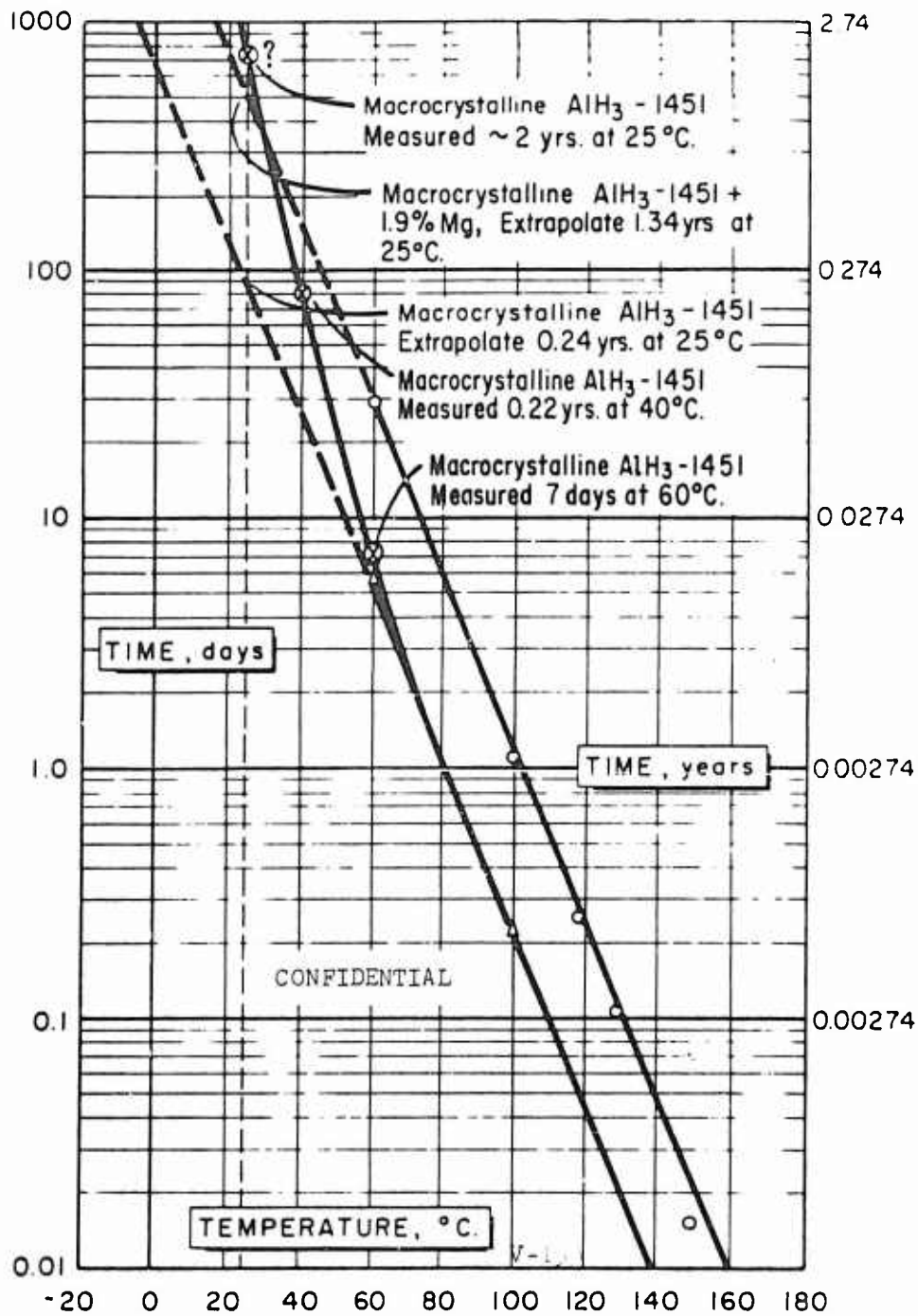
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Table XXVI

(C) Summary of Hydrogen Values for Macrocrystalline Aluminum Hydride-1451 Samples Stored at Ambient Temperature and -15°C.

Sample Number	Time, Months	Wt. % Hydrogen		Sample Number	Time, Months	Wt. % Hydrogen	
		Storage Temperature Ambient	Storage Temperature -15°C.			Storage Temperature Ambient	Storage Temperature -15°C.
3655-85	0	10.12	10.12	02034A	0	9.75	9.75
	20	9.70	9.94		3	9.50	9.58
	25	9.78	9.96		10	9.68	9.78
	31	9.84	9.92		15	9.67	9.87
	37	9.60	9.92		21	9.84	9.81
					27	9.78	9.83
		Average	9.97			Average	9.77
02044	0	9.86	9.86	02044A	0	9.83	9.83
	3	9.38	9.60		3	9.83	9.85
	10	9.82	9.89		10	9.87	9.91
	15	9.82	9.90		15	9.85	10.01
	21	9.86	9.88		21	9.92	10.00
	27	9.83	9.88		27	9.77	9.82
		Average	9.83			Average	9.91
02134A	0	9.84	9.84	03294	0	10.0	10.00
	3	9.93	9.86		9	10.08	9.99
	10	9.83	9.87		14	9.91	10.08
	15	9.83	9.82		20	10.01	10.06
	21	9.84	9.91		26	9.98	9.85
	27	9.93	9.86				
		Average	9.86			Average	10.00
04194	0	10.27	10.27	06014A	0	10.00	10.00
	8	9.94	9.96		6	9.96	10.02
	13	9.99	10.03		11	9.91	9.94
	19	9.89	9.97		17	9.93	10.02
	25	10.02	10.18		23	9.95	9.79
		Average	10.08			Average	9.95
06024A	0	9.89	9.89	06054	0	9.88	9.88
	6	10.08	10.03		6	9.98	9.92
	11	9.94	9.99		11	9.97	9.99
	17	9.90	10.03		17	10.02	10.03
	23	10.02	10.12		23	9.95	10.11
		Average	10.01			Average	9.99
06104A	0	9.89	9.89	06104AT	0	9.90	9.90
	6	10.07	10.02		6	10.01	9.99
	11	9.97	10.05		11	10.03	10.04
	17	10.10	9.96		17	9.99	10.09
	23	10.01	10.10		23	10.06	9.94
		Average	10.00			Average	9.99
07084	0	10.04	10.04	07084T	0	9.88	9.88
	5	10.05	10.00		5	10.07	10.05
	10	9.97	9.99		10	9.95	10.02
	16	9.94	9.99		16	9.88	9.96
	22	10.03	10.02		22	9.91	10.05
		Average	10.00			Average	9.99

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(C) Fig. 37 - Time Required for Aluminum
Hydride-1451 to Reach 1% Decomposition

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hydride after 0.24 year and approximately 1.34 years for hydride containing 1.9% magnesium. However, recent experimental data obtained from long-term surveillance studies of macrocrystalline AlH_3 -1451 show that the hydride is much more stable at lower temperatures than originally predicted.

Table XXVII

(C) Summary of Long-Term Storage Stability
of Aluminum Hydride-1451 at Ambient Temperature^a

<u>Sample Number</u>	<u>Age, years</u>	<u>% Decomposition</u> ^b
3655-85 ^c	3.1	2.8
02034A	2.3	0.3
02044	2.3	0.2
02044A	2.3	1.0
02134A	2.3	None
03294	2.2	0.5
04194	2.1	1.8
06014A	1.9	0.2
06024A	1.9	0.5
06054	1.9	None
06104A	1.9	None
06104AT(VCN) ^d	1.9	None
07084	1.8	0.2
07084T(VCN)	1.8	1.0

^aNo decomposition detected when stored at -15°C.

^bDetermined by carbon and hydrogen analysis; hydrogen $\pm 1\%$ of total.

^cLaboratory composite.

^dVCN - Acrylonitrile treated.

(C) Six lots of macrocrystalline AlH_3 -1451, which originally averaged 7 days to reach 1% decomposition at 60°C. were stored at 40°C., where they required approximately 80 days to reach the same level of decomposition. The same type of normal macrocrystalline hydride has been stored at ambient temperature for nearly two years, and, although an accurate measurement is difficult, it is estimated that they are approaching the 1% level of decomposition (see Section D.1.b.). The solid line drawn through the experimentally determined points at ambient (25°C.), 40°, and 60°C. shows considerable curvature (Figure 37) and a decrease in the decomposition rate from that originally predicted; this may be related to the "aging" phenomenon now being studied. It will be very interesting to determine when

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the magnesium-doped samples of AlH_3 -1451 currently under test will reach 1% decomposition at 40°C . It is expected, due to the enhancement of the "aging" effect by the incorporation of magnesium into the crystal lattice, that the lattice stabilized and/or DPA-treated hydride will possess greatly superior stability at the lower temperatures (25°C . and 40°C .). It should be noted that the original relationship represented by the time for the magnesium-doped AlH_3 -1451 to reach 1% decomposition at the various temperatures represents measured decomposition rates of a freshly prepared sample and for that reason does not take into consideration the "aging" phenomenon.

(C) The same eight lots of magnesium-doped hydride under surveillance at 40°C . as listed in Table XXV are also being stored for long-term surveillance. In addition, four of the above lots of magnesium-doped hydride are being stored in a modified Taliani apparatus at ambient temperature to continuously monitor their decomposition rates. The available data from these samples are presented in Table XXVIII. The samples range in magnesium concentration from 0.48% to 0.81%. Sample 01216 was lost after 120 days due to equipment failure. The average decomposition rate obtained is plotted in Figure 38. It is obvious that an acceleration of decomposition is being observed with increasing time, although the total decompositions of the hydride is only 0.1% in 200 days. A laboratory sample of normal macrocrystalline in situ DPA-treated sample was also placed on test. Its rate of decomposition is presently greater than that observed from the magnesium-doped lots, although its rate of decomposition appears to be decreasing. A total of 0.069% decomposition was observed after 120 days.

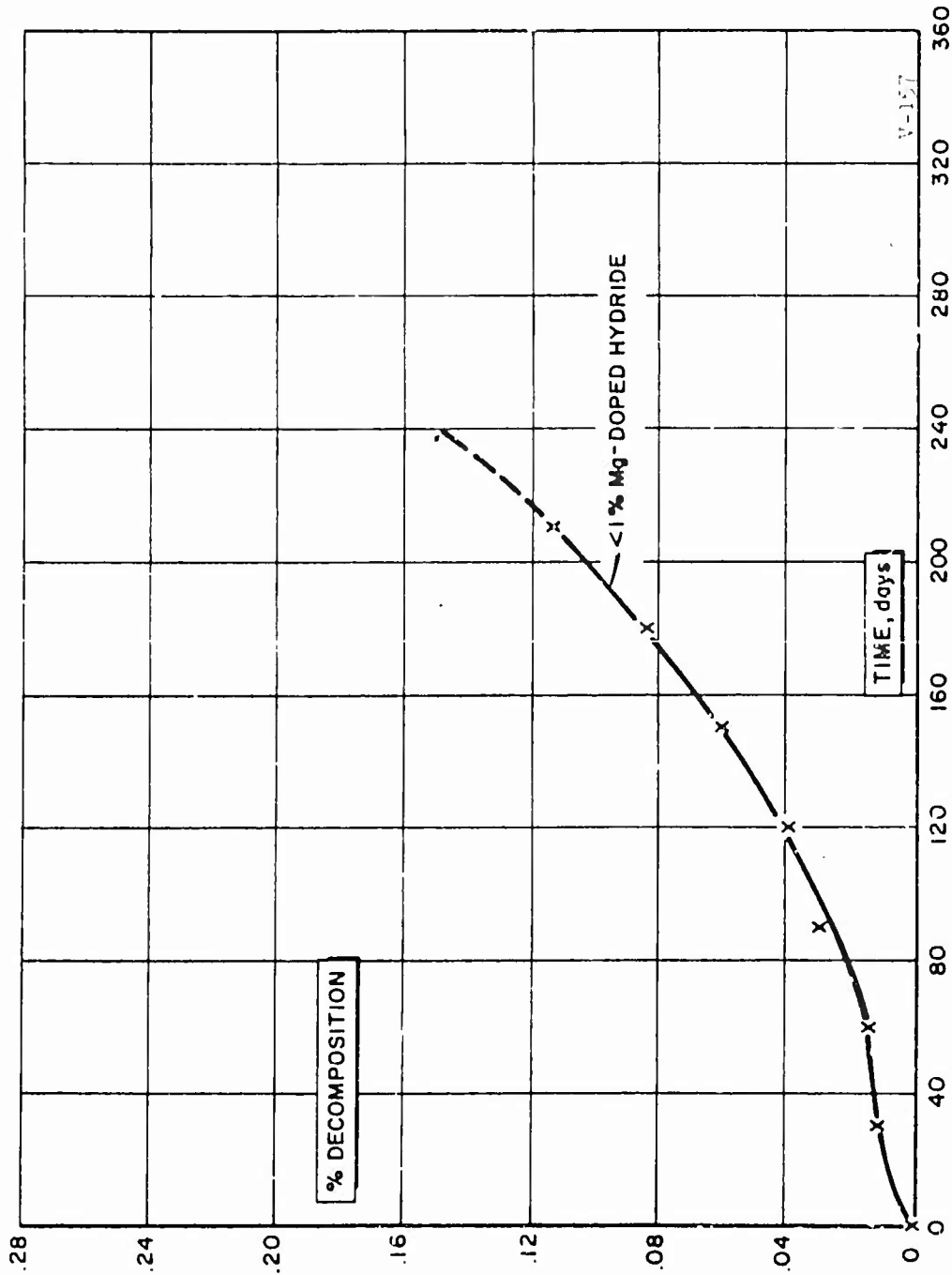
Table XXVIII

(C) Decomposition Rate of Magnesium-Doped Aluminum Hydride-1451 Stored at Ambient Temperature

Sample Number	% Mg	% Decomposition						
		Storage Time, days						
		30	60	90	120	150	180	210
01206	0.60	0.012	0.015	0.034	0.045	0.066	0.088	0.119
01216	0.67	0.010	0.017	0.022	0.035	---	---	---
01286	0.48	0.009	0.012	0.028	0.037	0.058	0.082	0.125
01316	0.81	0.012	0.012	0.033	0.040	0.056	0.080	0.095
Average %		0.011	0.014	0.029	0.039	0.060	0.083	0.113
9367-134 (Normal Macrocrystalline + DPA)		0.034	0.046	0.064	0.069			

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(C) Fig. 38 - Average Decomposition Rate
Magnesium-Doped Aluminum Hydride-1451 at 25°C.

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E. COMPATIBILITY AND FORMULATABILITY STUDIES (U)

(C) Samples of various types of aluminum hydride, including macrocrystalline, surface hydrolyzed, magnesium-doped, and in situ DPA-treated magnesium-doped AlH_3 -1451 have been evaluated at 25°C. and 40°C. in double base and composite propellant. Similar studies have been made at 60°C. with the addition of "aged" magnesium-doped AlH_3 -1451. The effect of adding water and DPA to the propellant mix has also been examined.

(U) The decomposition rate of samples was determined by measuring the gas evolved from propellant samples containing 0.25 g. of hydride in a modified Taliani apparatus.

1. Double Base Propellant (U)

(C) The studies on the behavior of AlH_3 -1451 in double base propellant have utilized both the ABL and Lockheed formulations as shown in Table XXIX; differing mainly in the nitroplasticizers used.

Table XXIX

(U) Double Base Propellant Formulations

<u>Ingredient</u>	<u>Composition, wt. %</u>	
	<u>ABL</u>	<u>Lockheed</u>
LMH-1	25.0	20.80
AP	26.0	30.69
PCNC	12.0	12.86
TEGDN	4.4	13.02
BDNPA	4.4	---
2-NDPA	1.0	---
Resorcinol	1.0	0.50
TMETN	---	21.63
Ethyl Centralite	---	0.50
NG	26.2	---

(U) Only the ABL double base formulation was used the first half of 1966, while both formulations were used during the second half of the year.

a. Storage at 25°C. (U)

(U) The gas generation rates of propellant samples under surveillance at 25°C. were monitored. Three of these samples were

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placed under surveillance in 1965 and three during 1966. A summary of the results from these tests is given in Table XXX. The date study was initiated, days on test, and percent decomposition, are given for each sample as of December 23, 1966.

Table XXX

(U) ABL Double Base Propellant Samples on 25°C. Surveillance Test

Date on Test	Sample Composition	Status as of 12-23-66	
		Days Elapsed	% Decomposition
8-4-65	Aluminum (Reference)	275	0
8-4-65	AlH ₃ -Lot 02055	508	0.33
10-13-65	AlH ₃ -Lot 02055, surface hydrolyzed	423	0.33
5-20-66	AlH ₃ -Lot QX-020, Mg-doped	217	0.088
6-6-66	AlH ₃ - Sample 8262-145, Mg-doped, <u>in situ</u> DPA-treated	190	0.090
6-7-66	AlH ₃ - Sample 9367-62, Mg-doped, <u>in situ</u> DPA-treated	199	0.086

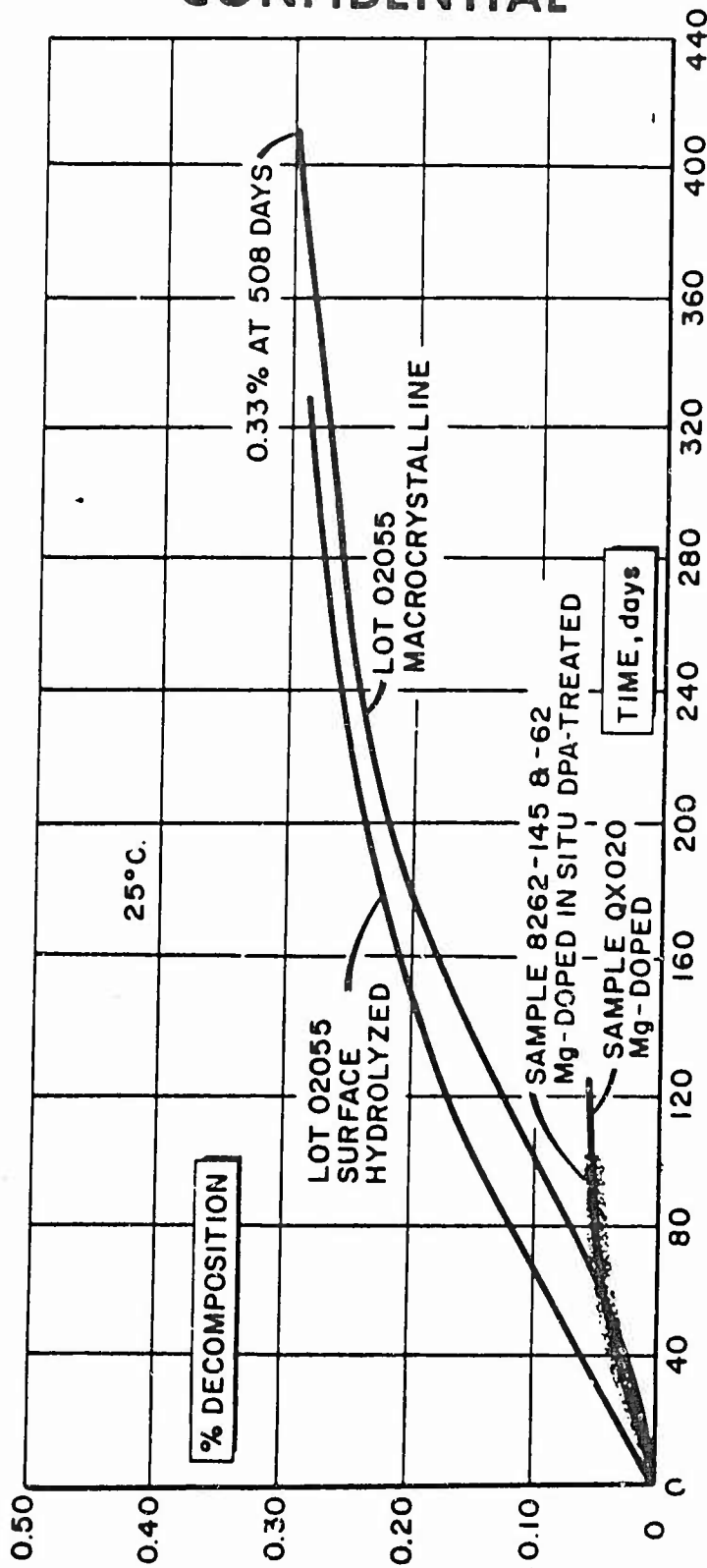
(U) The 25°C. surveillance samples continue to decompose very slowly. The decomposition curves of these samples are shown in Figure 39. The standard macrocrystalline AlH₃-1451 (Lot 02055) has now been on test in double base propellant for more than one year. It reached 0.33% decomposition in 508 days at 25°C. Its decomposition rate increased over approximately 100 days before decreasing (Figure 39). However, since the first 250 days the decomposition rate has remained constant at 0.11% per year. The surface hydrolyzed sample has followed a similar pattern.

(C) The three samples of improved AlH₃-1451 (Lot QX-020 Mg-doped, Sample 8262-145 Mg-doped, in situ DPA-treated and Sample 9367-62 Mg-doped in situ DPA-treated) which were placed on test in double base propellant during the second quarter of this year show a marked improvement in thermal stability over standard AlH₃-1451. The magnesium-doped, in situ DPA-treated hydride shows a decomposition rate of 0.09% compared to 0.22% for the standard AlH₃-1451 after 200 days.

b. Storage at 40°C. (U)

(C) Six propellant samples are under surveillance at 40°C. A surface hydrolyzed sample which reached 1% decomposition in 264 days was discontinued as well as a magnesium-doped, "aged" AlH₃-1451 sample which showed erratic results. A list of the samples remaining on test at 40°C. is given in Table XXXI.

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(C) Fig. 39 - Decomposition Rate of Different Types of Aluminum Hydride-1451 in Double Base Propellant at 25°C.

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Table XXXI

(U) Propellant Samples on 40°C. Surveillance Test

Date on Test	Sample Composition	Status as of 9-19-66	
		Days Elapsed	% Decomposition
9-8-65	AlH ₃ - Lot 02055 ^a	471	0.69
4-14-66	AlH ₃ - Lot QX-020, Mg-doped ^a	254	0.57
6-8-66	AlH ₃ - Sample 9367-62, Mg-doped, <u>in situ</u> DPA-treated ^b	163	0.26
6-7-66	AlH ₃ - Sample 9367-62, Mg-doped, <u>in situ</u> DPA-treated ^a	199	0.27
6-6-66	AlH ₃ - Sample 8262-145, Mg-doped, <u>in situ</u> DPA-treated ^a	201	0.45
9-8-65	Aluminum (reference) ^a	470	Neg.

^aABL double base propellant formulation given in Section E.1.

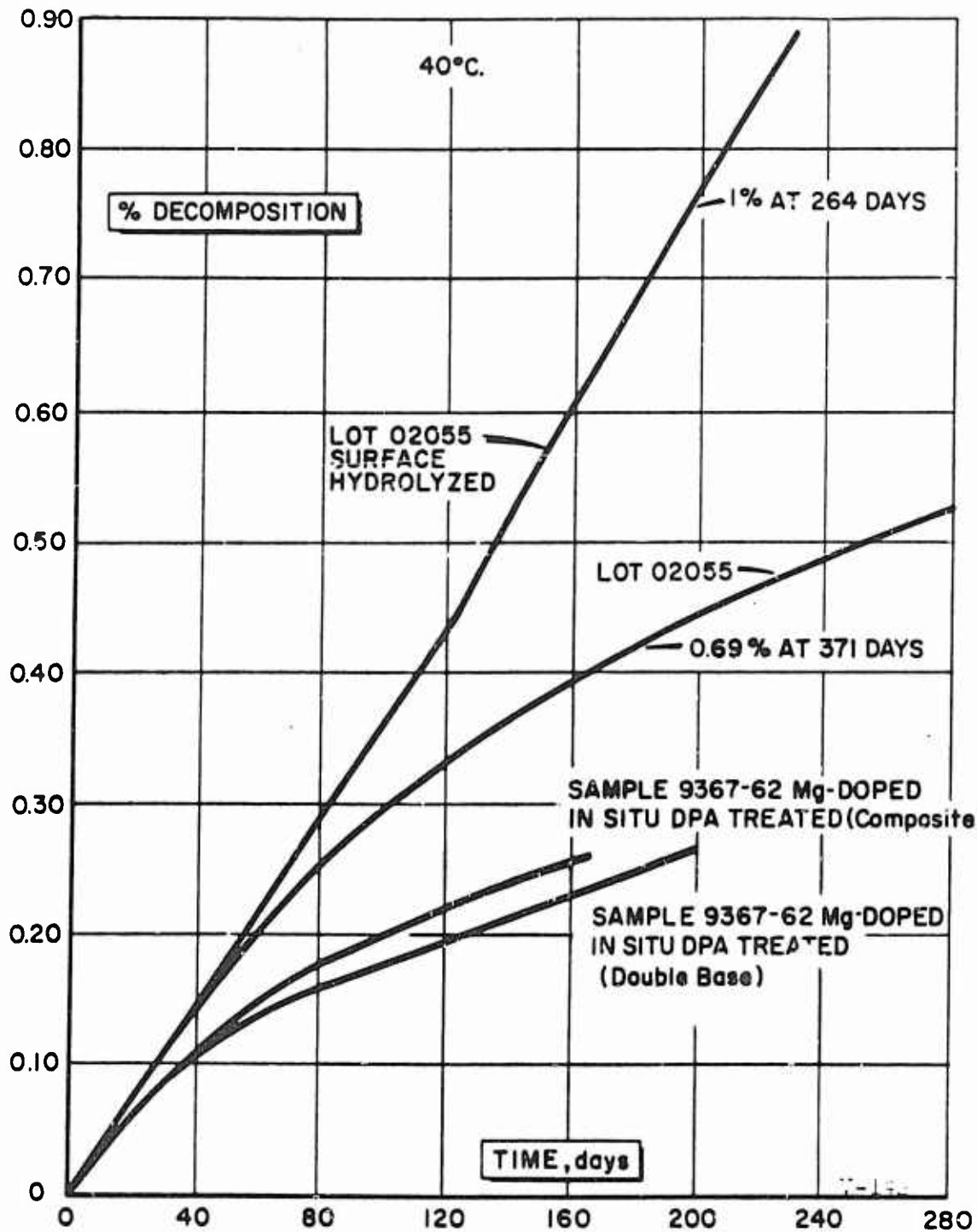
^bThiokol composite propellant formulation given in Section E.2.

(C) The benefit obtained from magnesium-doped, in situ DPA-treated, AlH₃-1451 compared to standard AlH₃-1451 is depicted in Figure 40. An approximate twofold improvement in stability is observed.

(C) The behavior of surface hydrolyzed AlH₃-1451 in double base propellant is of considerable interest, as most commercially available material possesses this type of surface to some degree. The surface hydrolyzed sample shown in Figure 40 maintained a constant rate of decomposition throughout the test period, reaching 1% decomposition in 264 days, corresponding to a decomposition rate of 1.38% per year. No decrease in decomposition rate occurred with the surface hydrolyzed sample, indicating the stabilizing effect of the double base propellant was ineffective at 40°C.

(C) Two of the samples which were on test at 40°C. in double base propellant have exhibited erratic behavior. These samples are (i) magnesium-doped in situ DPA-treated (8262-145), and (ii) magnesium-doped Lot QX-020 AlH₃-1451. Both of these samples previously exhibited remarkable stabilities at 60°C. and are showing excellent stability at 25°C. The cause of the erratic behavior at 40°C. is not known at this time.

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(C) Fig. 40 - Decomposition Rate of Different Types of Aluminum Hydride-1451 Propellant at 40°C.

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c. Stabilization of the Hydride by Double Base at 25°C. and 40°C. (C)

(C) Both the decreased decomposition rate of aluminum hydride and the poorer performance of the surface hydrolyzed aluminum hydride-1451 in double base propellant as observed from the 25°C. and 40°C. surveillance data, may be explained by a proposed double base stabilization theory. It is postulated that the decomposition products of the double base propellant matrix, primarily nitric oxide (NO), under certain conditions, act as an effective stabilizer for aluminum hydride. The generation of NO and the resultant stabilization of the AlH₃-1451 do not occur immediately, but take place over a period of time as shown by a slowly decreasing decomposition rate until a maximum stabilization effect occurs. The data also suggest that hydrolysis or oxidation of the surface of the AlH₃-1451 crystals produces a barrier to the stabilizing agent, NO, preventing effective stabilization.

(C) Data, presented in Table XXXII, show consistently less NO evolved from the AlH₃-1451 samples than from the reference samples containing aluminum. The samples were stored under an argon atmosphere from October 23, 1965 to March 21, 1966 before the gases evolved were analyzed by mass spectroscopy. These data indicate either the AlH₃-1451 is reacting with NO forming some compound, probably on the surface of the AlH₃-1451, or less likely, the AlH₃-1451 is inhibiting the formation of the NO. No consistent trend was observed for the formation of N₂O. Unfortunately, the extremely low concentrations of the individual gas species limit the accuracy of the data, and the results presented in Table XXXII must be interpreted with caution.

Table XXXII

(C) Gases Generated from Double Base Propellant Samples at 40°C.

<u>Gases Generated</u>	Amount of Gas, $\frac{\text{g. moles}}{\text{g. propellant}} \times 10^{-4}$			
	<u>Aluminum Sample 1a</u>	<u>Aluminum Sample 4a</u>	<u>Lot 02055H^a 1451</u>	<u>Lot 02055 1451</u>
H ₂	1.24	1.28	68.50	21.10
H ₂ O	1.13	2.71	2.59	2.68
CO	0.37	0.52	0.64	0.81
N ₂	N11	0.93	0.58	0.94
NO	0.66	0.48	0.31	0.36
Mass 43 ^b	0.05	0.17	0.11	0.04
N ₂ O	1.08	0.51	0.86	0.15
Mass 45 ^b	0.33	0.07	0.11	0.38

^aIndicates surface hydrolyzed.

^bInsufficient quantities of these fragments prevent identification.

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(C) Contrary to some reported data (11), a considerable amount of experimental data as summarized below, supports the conclusion that double base propellant stabilizes AlH_3 -1451.

- (1) AlH_3 -1451 is consistently more stable in the presence of double base propellants than when neat (usually by a factor of two).
- (11) AlH_3 -1451 recovered from "aged" double base propellant showed the presence of a surface coating on the crystals which contained nitrogen and oxygen (1).
- (111) Nitric oxide (NO) is a decomposition product from ingredients present in the double base system as determined by off-gas analysis.
- (iv) Early laboratory work has independently demonstrated the stabilizing effect of NO on AlH_3 -1451 (3).
- (v) Recent analysis of the gases generated by double base samples has shown less NO evolved from those samples containing AlH_3 -1451 than those containing aluminum (see Table XXXII).
- (vi) Neat surface hydrolyzed AlH_3 -1451 shows improvement in stability over standard AlH_3 -1451 but when formulated in double base propellants is less stable than the standard (Figures 39 and 40).

d. Storage at 60°C. (U)

(C) Twenty-two double base propellant samples studied for compatibility and formulatability at 60°C. are listed in Table XXXIII. The results from these samples provide an evaluation of: (i) magnesium-doped, (ii) "aged", magnesium-doped, (iii) magnesium-doped, in situ DPA-treated, and surface hydrolyzed AlH_3 -1451. In addition, the effect of adding water and DPA to the propellant mix was examined. Three reference samples of propellant containing aluminum and four samples containing AlH_3 -1451 (both double base and composite) remain on test.

(C) Most of the propellant studies at 60°C. have been conducted with the ABL formulation. Recent evaluation of two selected AlH_3 -1451 samples in the Lockheed formulation (Lot QX-020, magnesium-doped and Sample 9357-62, magnesium-doped, in situ DPA-treated) show very close agreement with the results previously obtained in the ABL formulation.

(C) Table XXXIV shows the decomposition rate of seven propellant samples at 60°C. using the ABL double base formulation. Six

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of these contained magnesium-doped AlH_3 -1451 while the other contains aluminum as a reference. It has shown no significant gassing in 103 days at 60°C . Figure 41 illustrates the remarkable stabilities displayed by three of these samples. Magnesium-doped "aged", and magnesium-doped, in situ DPA-treated samples of AlH_3 -1451 continue to show nearly a tenfold improvement over standard AlH_3 -1451.

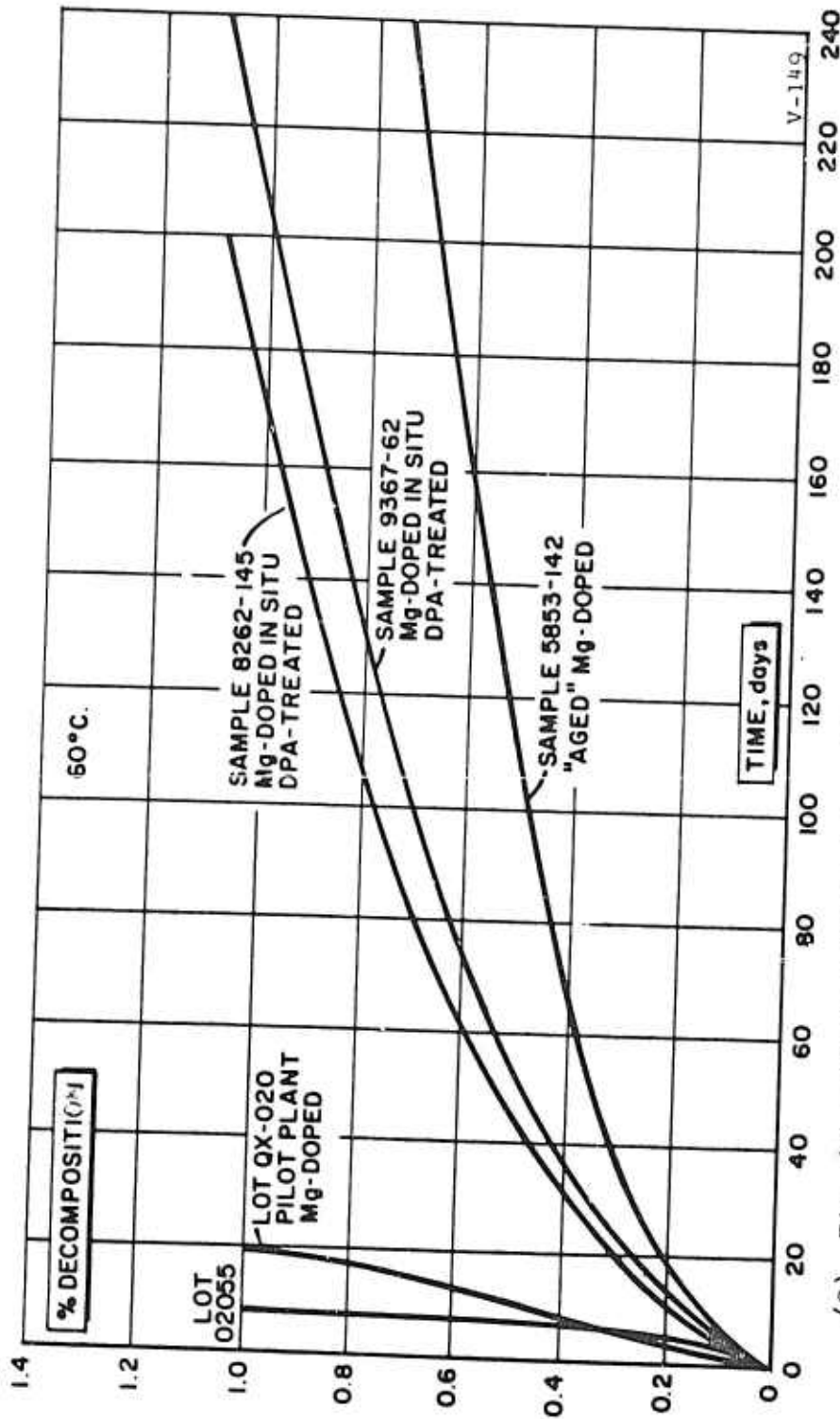
Table XXXIII

(U) Identification of Double Base Propellant Samples
on 60°C . Taliani Test

Number	Double Base Formulation	Fuel Type
1	ABL	Sample 8262-145; Mg-doped, <u>in situ</u> DPA-treated
2 ^a	ABL	Sample 5853-142; Mg-doped, "aged".
3	ABL	Sample 9367-61; Mg-doped, <u>in situ</u> , DPA-treated
4	ABL	Sample 9367-62; Mg-doped, <u>in situ</u> , DPA-treated
5	ABL	Sample 04126; Mg-doped
6	ABL	Sample 9026-22; "aged", Mg-doped
7	ABL	Sample 9569-16A; fresh
8	ABL	Sample 9569-16B; surface hydrolyzed, 0.31%
9	ABL	Sample 9569-16C; surface hydrolyzed, 0.41%
10	Lockheed	Texas P. P. Lot QX-020; Mg-doped
11 ^a	Lockheed	Aluminum (reference).
12 ^a	ABL	Aluminum (reference)
13	Lockheed	Sample 9367-62; Mg-doped, <u>in situ</u> DPA-treated
14	Lockheed	Lot 02055 Standard
15	ABL	Texas P. P. Lot 05106; Mg-doped
16	ABL	Texas P. P. Lot 05066; Mg-doped
17	ABL	Texas P. P. Lot 05196; Mg-doped
18	ABL	Texas P. P. Lot 05136; Mg-doped
19	ABL	Lot 02055 Standard, +1% DPA
20	ABL	Lot 02055 Standard
21 ^a	ABL	Lot 02055 + 0.25% H_2O
22 ^a	ABL	Lot 02055 + 0.50% H_2O

^aRemain on test as of December 23, 1966.

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(C) FIG. 41 - Decomposition Rate of Magnesium-Doped, "Aged", and Magnesium-Doped, in situ DPA-Treated Aluminum Hydride-1451 in Double Base Propellant at 60°C.

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Table XXXIV

(C) Accelerated Testing of ABL Double Base Propellant
Containing Aluminum Hydride-1451 at 60°C.

<u>Type of AlH₃-1451 Fuel</u>	<u>Days to Reach 1% Decomposition</u>
Sample 8262-145; Mg-doped, <u>in situ</u> DPA-treated	170
Sample 5853-142; Mg-doped, "aged" ^a	0.74 after 243 days
Sample 9367-61; Mg-doped, <u>in situ</u> DPA-treated	70
Sample 9367-62; Mg-doped, <u>in situ</u> DPA-treated	225
Sample 04126, Mg-doped	23
Sample 9026-22; "aged", Mg-doped, DPA-treated	18
Aluminum reference ^a	--

^aRemain on test as of December 23, 1966.

(C) Data obtained from magnesium-doped, pilot plant AlH₃-1451 samples in double base propellant at 60°C. are shown in Figure 42. Considerable variation from lot to lot has been observed. However, all magnesium-doped samples were equal or better than standard AlH₃-1451. Four of the six magnesium-doped samples required 16 days or more to reach 1% decomposition compared to 8 days for the standard hydride, representing a twofold improvement.

e. Effect of Surface Hydrolysis (U)

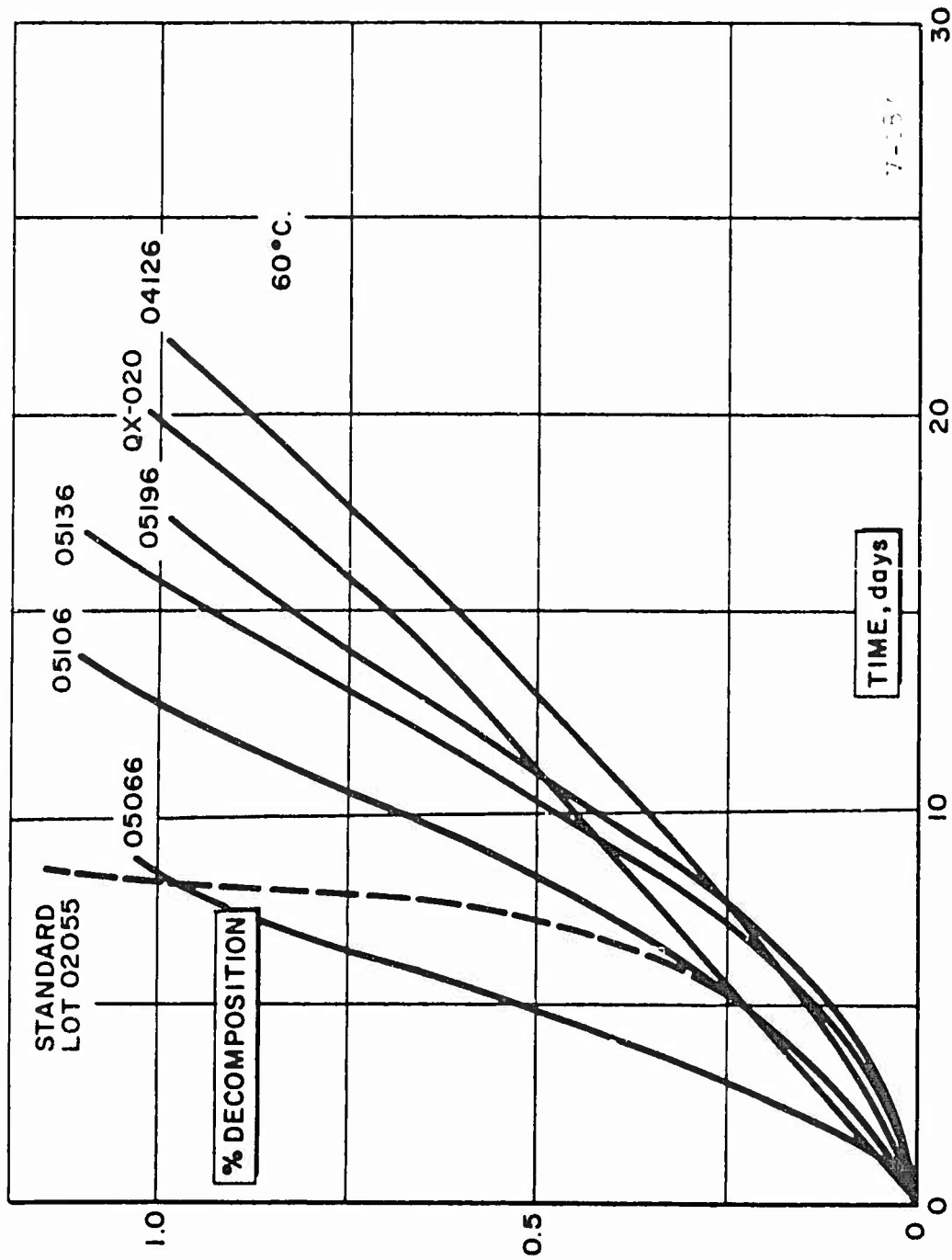
(C) The effect of surface hydrolysis and water on the stability of AlH₃-1451 in propellant is not clearly understood. An initial experiment was conducted to more accurately define the effect of surface hydrolysis, but failed to give reliable results when Taliani equipment problems developed. The experiment was repeated with two portions of a different sample hydrolyzed 0.3% and 0.41%. These data are presented in Figure 43.

(C) The surface hydrolyzed hydride shows a significant amount of initial gassing followed by approximately a twofold stabilization of the hydride as compared to fresh surface hydride in the same double base propellant formulation. These results disagree with the observed poorer performance of surface-hydrolyzed material at 25°C. and 40°C. shown in Figures 39 and 40.

f. Effect of Direct Addition of DPA to Double Base Propellant (C)

(C) Figure 44 shows the effect of adding 1% DPA to the propellant mix. It indicated no initial effect, but did retard the

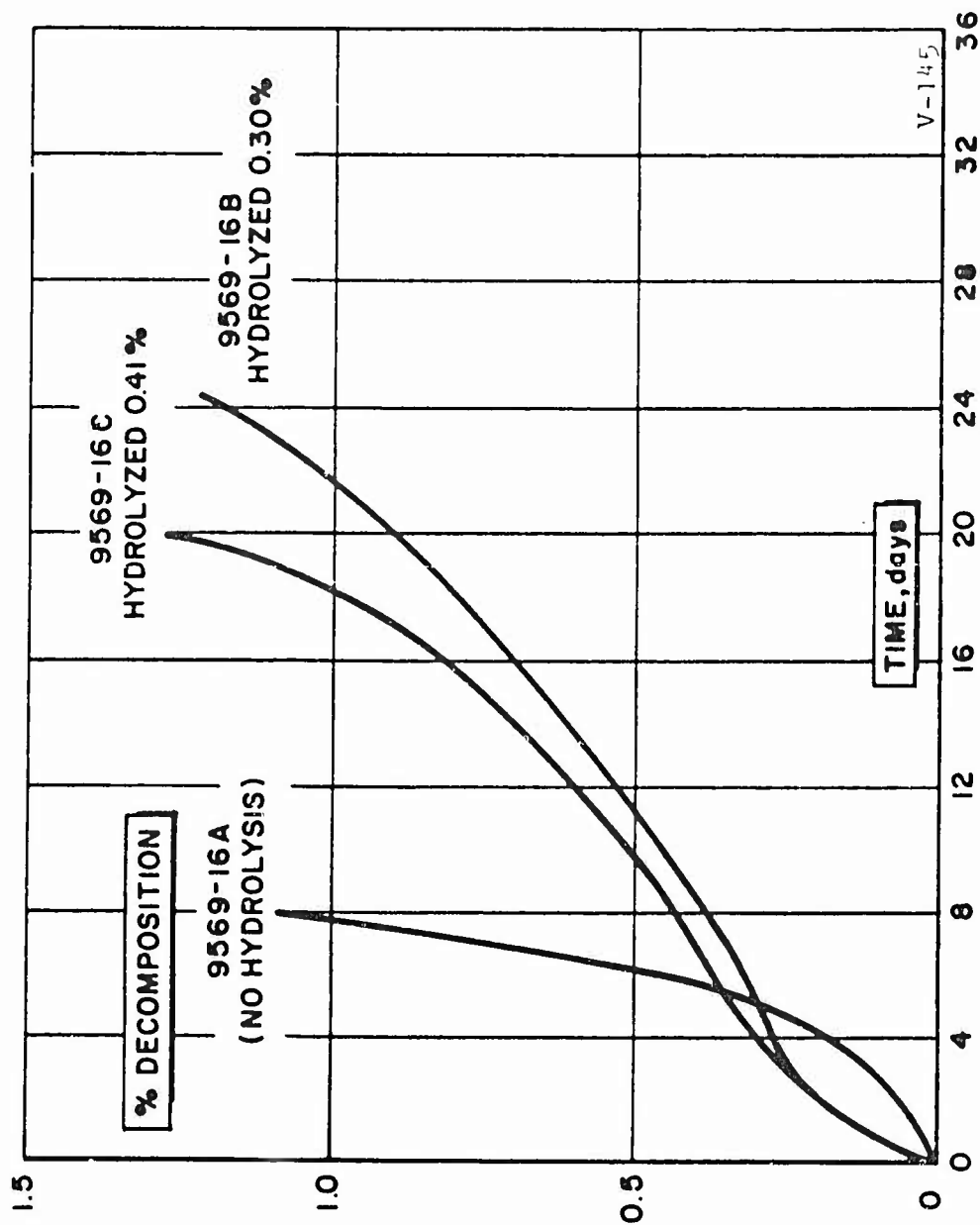
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(7) Fig. 42 - 60°C. Italian Results from Magnesium-Doped Aluminum Hydride-1451 in Double Base Propellant.

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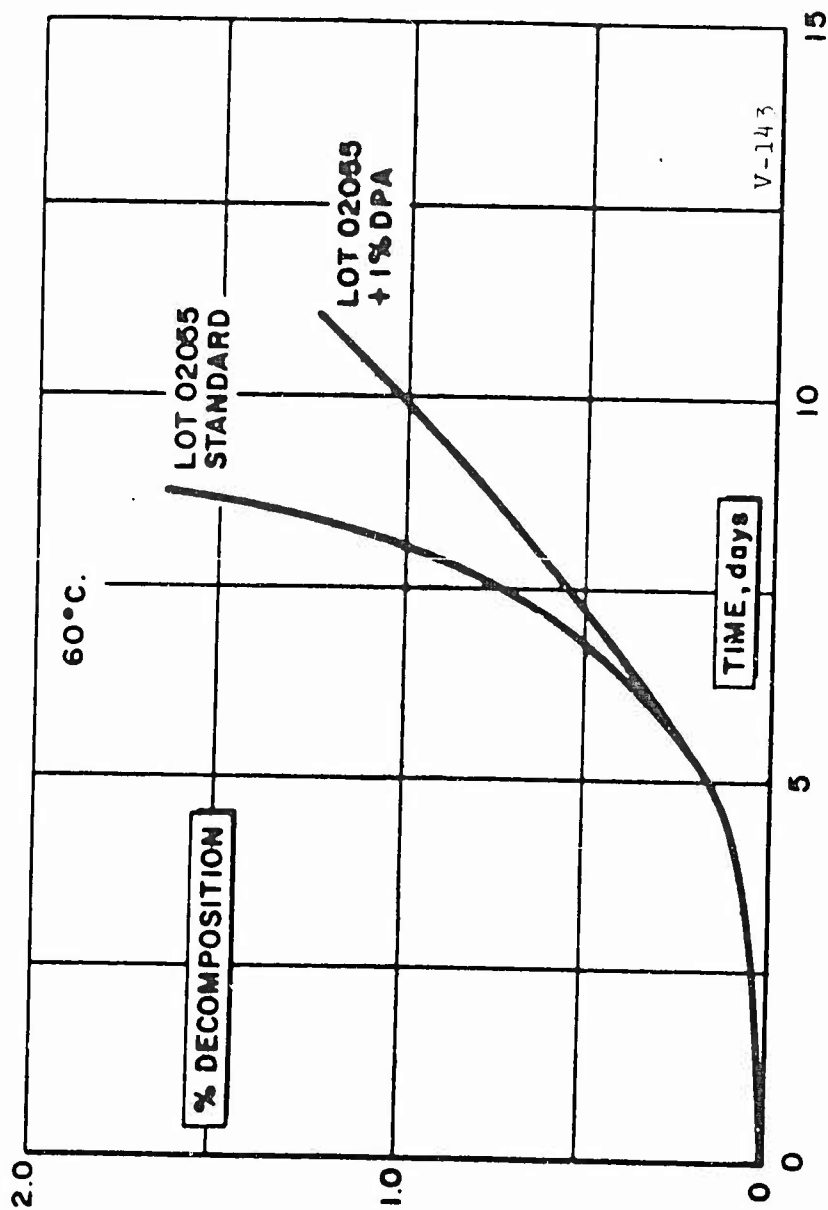
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(C) FIG. 43 - Surface Hydrolyzed Aluminum Hydride-1491
In ABL Double Base Propellant at 60°C.

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(C) Fig. 44 - 60°C. Taliari Results from a Study of DPA Added to Double Base Propellant Containing Aluminum Hydride-1451

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accelerated decomposition of the AlH_3 -1451 after the first five days. The application of the DPA on the surface before drying the hydride appears to be necessary if it is to be beneficial in double base propellant.

g. Effect of Direct Addition of Water to Double Base Propellant (U)

(C) Carefully controlled amounts of water added to the propellant mix appear to have a very significant stabilizing effect on the double base propellant. Figure 45 shows the stability obtained by adding 0.25% and 0.50% water directly to the AlH_3 -1451 double base propellant mix. This small addition of water resulted in an unexpected twentyfold improvement in stability over the same formulation containing no water. In addition, no significant initial gassing was encountered. Further work should be conducted to define the actual mechanism of this phenomenon.

2. Composite Samples Containing Aluminum Hydride-1451 (C)

(U) The Thiokol formulation was used in all composite propellant samples evaluated at 60°C. during 1966. This formulation is given in Table XXXV.

Table XXXV

(U) Thiokol Composite Propellant Formulation

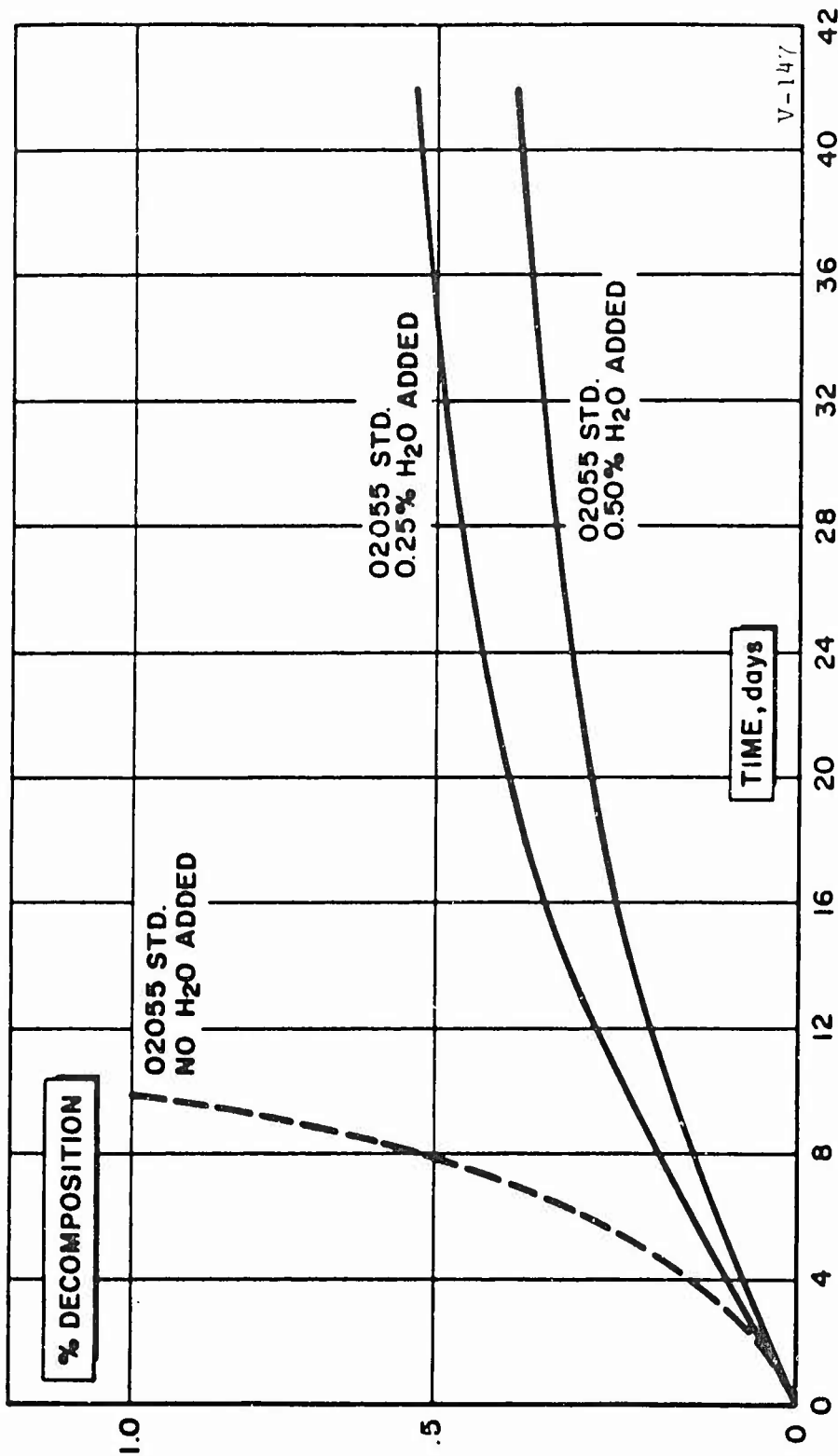
<u>Ingredient</u>	<u>Composition, wt. %</u>
LMH-1	25.0
AP	49.5
TMETN	14.0
ZL-437	10.11
HX-874	1.39

(U) The nine composite samples listed in Table XXXVI were studied for compatibility and formulatability. Of these only the aluminum standard remains under surveillance.

(C) Figure 46 shows the decomposition of standard and magnesium-doped AlH_3 -1451 both neat and in composite propellant; the magnesium-doped sample exhibits more than a twofold improvement over the standard AlH_3 -1451.

(C) Figure 47 shows the results obtained with six pilot plant lots of magnesium-doped AlH_3 -1451 in composite propellant compared to the standard (Lot 02055). These results are very similar to those shown in Figure 42 for double base propellant. Excellent stabilities were observed with all magnesium-doped samples which exhibited better than a twofold improvement over standard AlH_3 -1451.

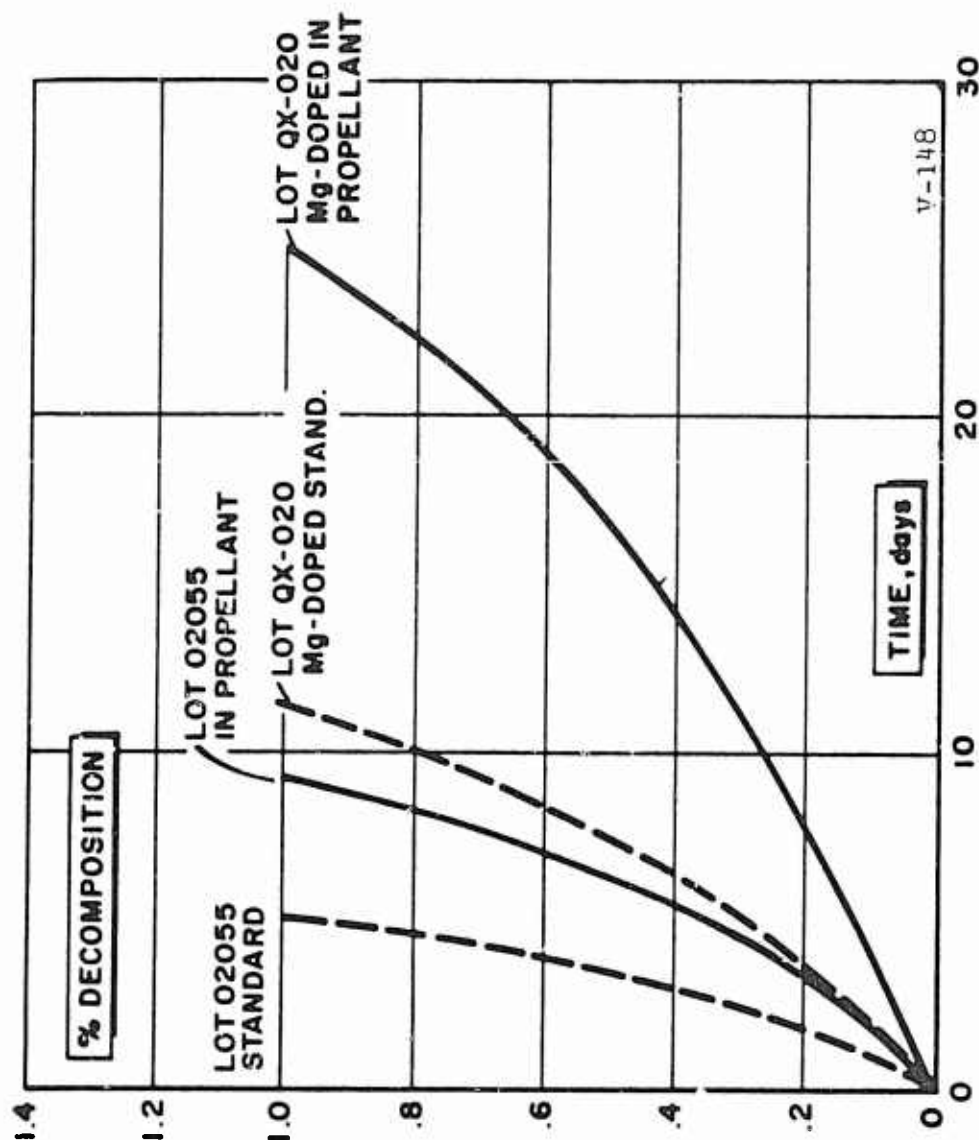
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(C) Fig. 45 - 60°C. Taliani Results from a Study of Water Added to Double Base Propellant Containing Aluminum Hydride-1451

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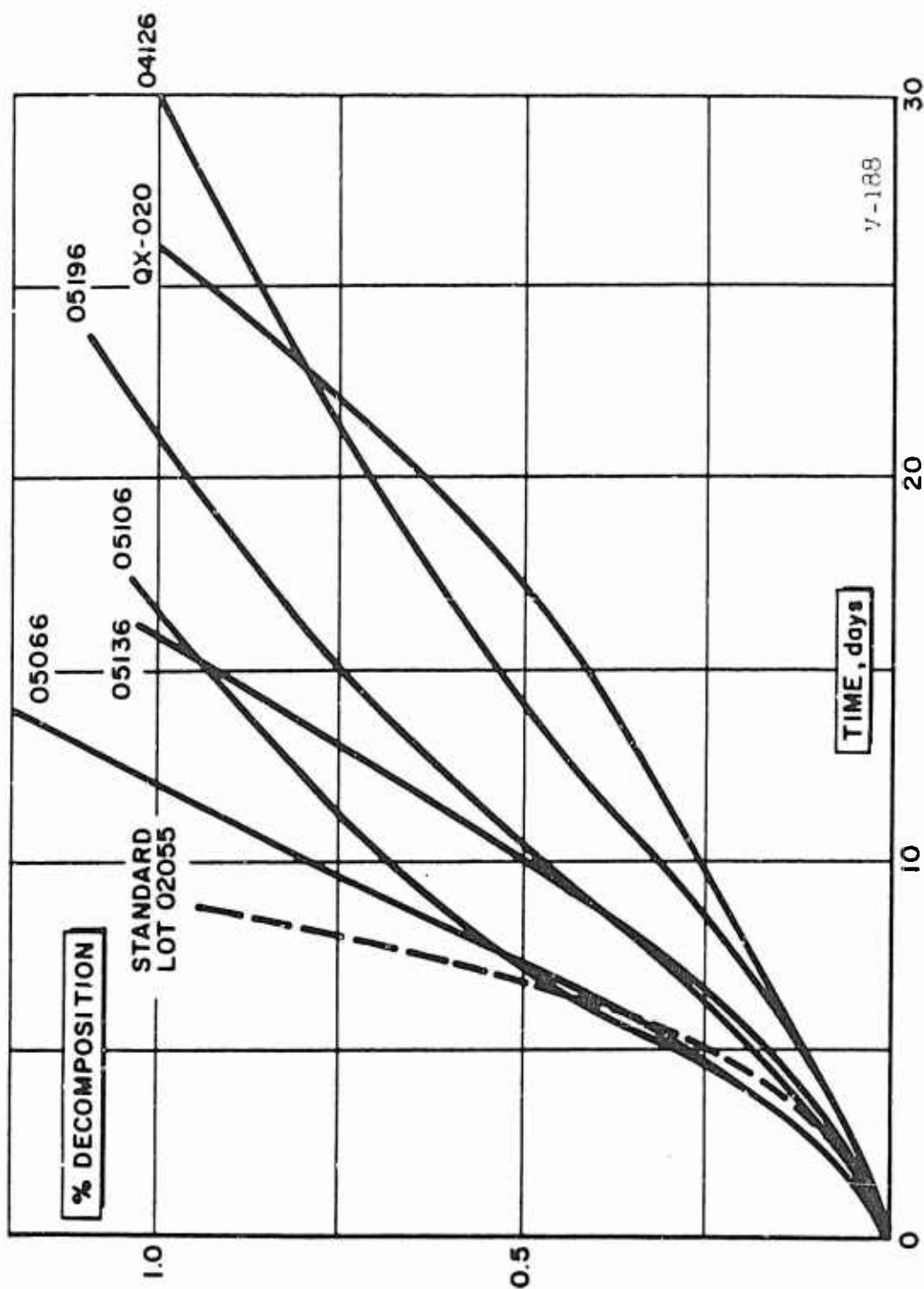
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(C) FIG. 46 - 60°C. Taliani Results of Standard and Magnesium-Doped Aluminum Hydride in Composite Propellant

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(C) Fig. 47 - 60°C. Italiani Results from Magnesium-Doped Aluminum Hydride-145i in Composite Propellant

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(C) A magnesium-doped, in situ DPA-treated AlH_3 -1451 continued to demonstrate remarkable stability as shown in Figure 48. The sample decomposed only 0.84% after 91 days at 60°C . However, due to equipment problems, the test had to be terminated. The sample demonstrated approximately a tenfold improvement in stability over standard AlH_3 -1451.

F. MISCELLANEOUS PROPELLANT STUDIES (U)

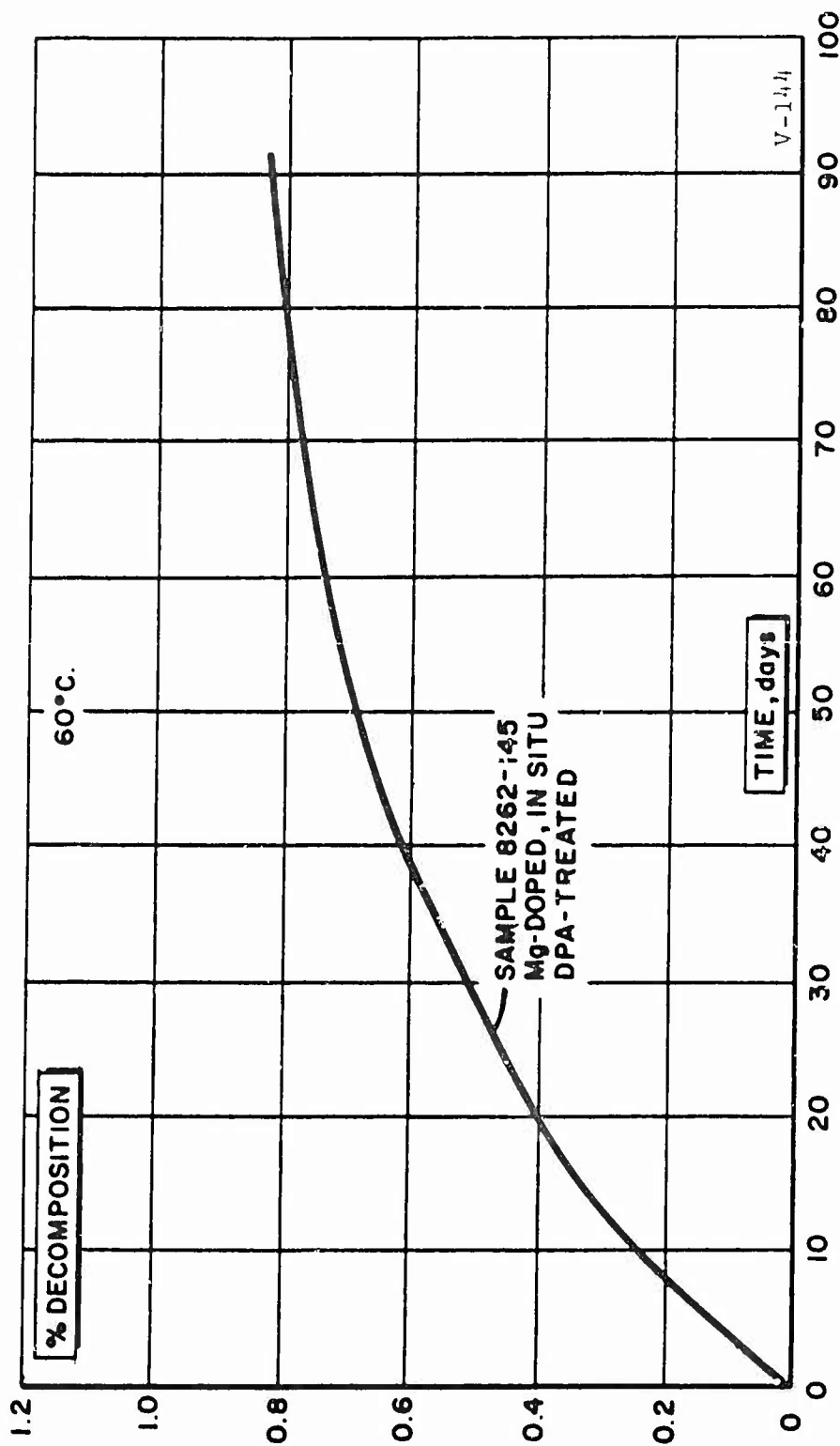
(C) The recent improvement in the stability of AlH_3 -1451 has reduced many of the problems preventing the use of this fuel as a high energy rocket propellant ingredient for controlled environmental missile applications. The actual rate of decomposition which might be tolerated in a solid rocket motor could be limited by the internal structural failures in the grain resulting from points of high gas pressure. This problem exists for any propellant ingredient which is capable of decomposing and generating gas. Lockheed Propulsion Company is currently studying this area (12).

(C) The specific problem created by AlH_3 -1451 is related to the thermal stability of the compound. Recent advances which have resulted in very stable AlH_3 -1451 should drastically reduce the quantities and rate of gas generation in propellant formulations.

(C) The magnitude of the problem of grain failure caused by gas generation in the grain is not known. The diffusivity through the propellant of the gas generated has a very large effect on the amount of gas generation which can be tolerated. Hydrogen readily diffuses through most substrates.

(C) A Dow technique for determining permeabilities of various substrates, primarily plastics, was used to provide some insight into the rate of diffusion of H_2 through propellant containing AlH_3 -1451. The procedure involved placing a propellant sample between an atmosphere of hydrogen and an atmosphere of tritium, and measuring the rate of transfer of the radioactive tritium with a standard detecting device (Figure 49). This single experiment gave a value of the diffusivity of H_2 through double base propellant of $D = 3.85 \times 10^{-4} \text{ cm}^2/\text{hr.}$ at 25°C . and one atmosphere. It should be emphasized that only one experiment was carried out to determine the feasibility of obtaining the desired results by this technique. The calculated diffusivity does not consider the possible exchange with other hydrogen containing compounds in the propellant grain and for that reason the value is only very preliminary and additional work would be required to resolve this question. The fundamental equipment used in this determination is shown in Figure 49.

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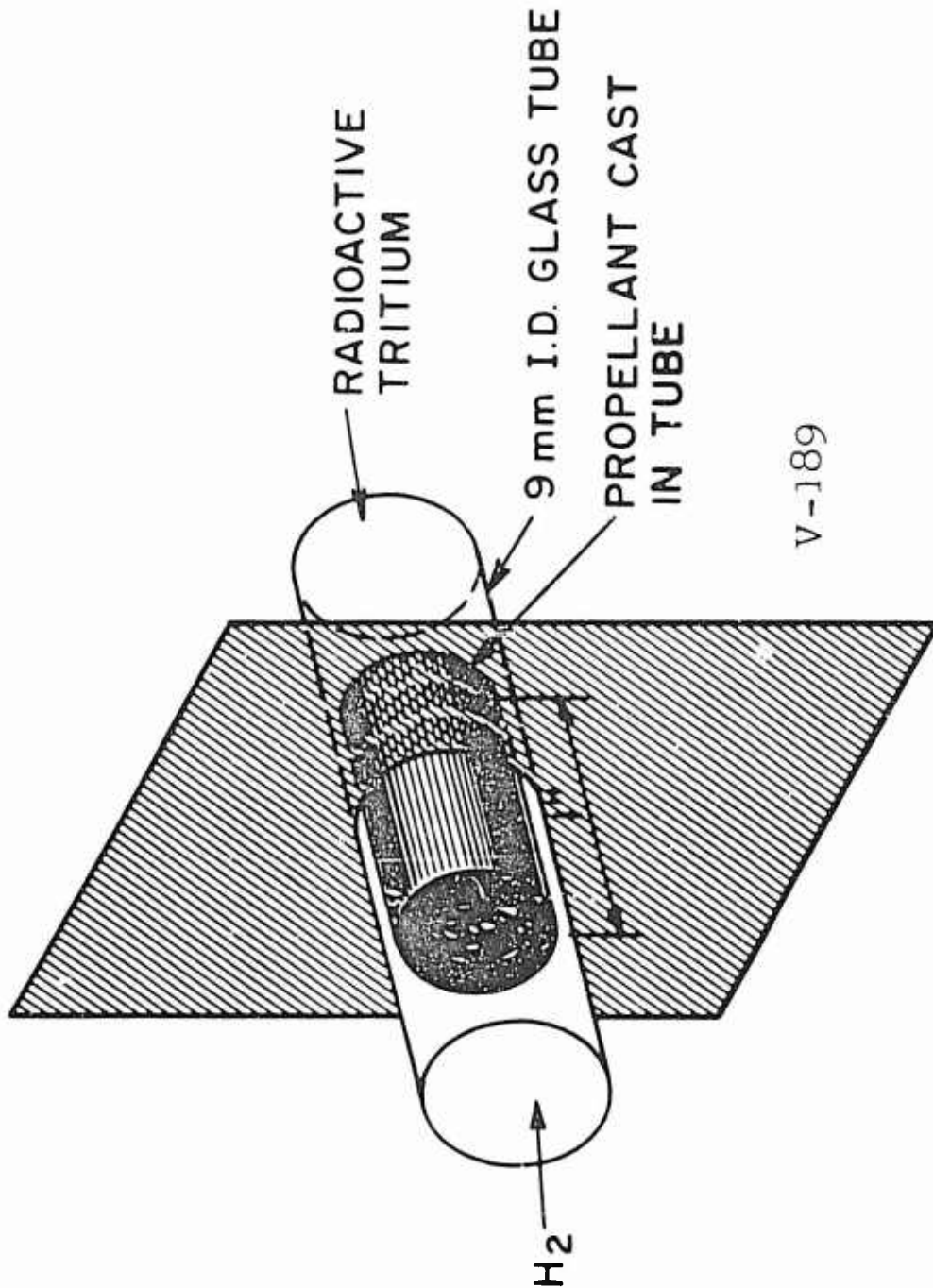


(C) Fig. 48 - 60°C. Taliani Results from Magnesium-Doped, in situ DPA-Treated Aluminum Hydride In Composite Propellant

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(V) FIG. 1 - Diagram of Diffusivity Apparatus

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SECTION IV

(U) CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS (U)

(C) Based on the results of this report period, the following recommendations are made:

- (i) The best technique for incorporating magnesium into the AlH_3 -1451 crystal is the addition of an ether solution of $\text{LiMg}(\text{AlH}_4)_3$ to the aluminum hydride feed solution.
- (ii) The incorporation of magnesium into the continuous process AlH_3 -1451 does not result in the same degree of improvement in stability as obtained by the batch process. The reason for this difference is not known, but it is believed to be associated with the manner in which magnesium is incorporated into the crystal faces of the hydride.
- (iii) Teflon FEP was shown to be a superior material of construction for an aluminum hydride crystallizer liner; in laboratory runs no adhesion or decomposition occurred. A similar improvement was not realized with a 9-gallon crystallizer; product adhered to the walls of this unit, but eventually broke away in sheets of AlH_3 -1451. This difference between the laboratory unit and the larger crystallizer is believed to be due to design changes which were necessary for fabricating the unit from stock FEP items.
- (iv) None of the materials of construction which have been evaluated is entirely acceptable; perfluoro-hydrocarbons appear to have the best potential.
- (v) Laboratory experiments with Teflon TFE and pyrex glass indicate that product adhesion during AlH_3 crystallization is more serious with higher inner wall temperatures. Adhesion may be considerably decreased or eliminated by maintaining lower wall temperatures and heating the solvent by internal means.
- (vi) The aluminum hydride crystalline phase obtained at nucleation is a direct function of specific nucleation conditions, such as aluminum hydride concentration, ether concentration (temperature) and lithium aluminum hydride concentration.

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- (vii) In the present art of AlH_3 crystallization, the ratio of nucleation rate to crystal growth rate is low, resulting in limited crystal surface area during the growth stage and, consequently, poor crystallinity.
- (viii) Preliminary laboratory work has demonstrated the concept of a continuous external nucleator system to supply nuclei of AlH_3 -1451 to a crystallizer unit.
- (ix) The most significant parameters in the AlH_3 -1451 crystallization process are agitation, crystal retention time, feed rate, and additive hydride concentrations; ether concentration (temperature) is important during nucleation.
- (x) The product rate of the tubular design AlH_3 -1451 crystallizer can exceed 0.06 moles/liter/hour (0.015 lb./gal./hr.).
- (xi) Decomposition is primarily related to the presence of impurities which also affect nucleation and growth.
- (xii) Post treatment of AlH_3 -1451 with DPA or water improves the thermal stability. Treatment techniques used to apply these agents are important.
- (xiii) The stoichiometric equivalence point of the reaction between aluminum chloride and lithium aluminum hydride can be routinely determined by flame photometry.
- (xiv) Incorporation of magnesium per se is not sufficient to guarantee stabilization of AlH_3 -1451. The process parameter(s) which controls the effectiveness of magnesium stabilization of AlH_3 -1451 has not been found.
- (xv) The density of magnesium-doped hydride decreases as magnesium concentration increases. The resulting structure is a substitutional solid solution, the magnesium substituting at random for aluminum atoms in the lattice.
- (xvi) The optimum stability of AlH_3 -1451 by DPA is obtained by in situ treatment in a wash solution containing 2-5 g. of DPA/250 ml. of benzene. An evaporation technique, whereby a known amount of an ether solution of DPA is dried on the product, is more effective for material made by the continuous process.

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- (xvii) DPA probably forms a weak adduct with AlH_3 -1451 through the triple bond. This inhibits the excessive build-up of electron density at any one point in the AlH_3 -1451 crystal.
- (xviii) DPA is a better stabilizing agent for AlH_3 -1451 than a number of other acetylenic derivatives and compounds containing one or more phenyl groups.
- (xix) Large improvements in stability result when AlH_3 -1451 is stored at -15°C .; several "aged" lots required nearly 100 days before reaching 1% decomposition at 60°C .
- (xx) The initial gas from "aged" samples contains large amounts of water vapor, which may play a major role in the "aging" process. It may be possible to reproduce the same stabilizing effect in much shorter periods of time by moisture and heat treatment.
- (xxi) Aluminum hydride-1451 is stabilized in the double base propellant formulation. This is probably due to a reaction between the hydride and nitric oxide.
- (xxii) Magnesium-doped, "aged", and magnesium-doped, in situ DPA treated AlH_3 -1451 show remarkable stability in double base propellant. The goal of less than 1% decomposition in one year at 60°C . is being reached by magnesium-doped, "aged" AlH_3 -1451 in double base propellant.
- (xxiii) The effect of water is not clearly understood. The process by which it is added to the AlH_3 -1451 seems to determine whether it is beneficial or detrimental to stability. Partial hydrolysis of the hydride prior to its use in propellant has not consistently resulted in a significant increase in stability. Recent work, however, with propellant formulations which contain carefully controlled quantities of water added to the mix indicate a many-fold improvement in stability can be achieved.

B. RECOMMENDATIONS (U)

(C) Based on analysis of results of this report period the following recommendations are made:

- (1) Studies to determine the effect of crystallizer wall temperature on adhesion should be continued. Currently, the most promising fluorocarbon liners should be investigated as possible materials of construction.

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- (11) Reasons why the stability of laboratory samples of AlH_3 -1451 made by the continuous process are not enhanced by the incorporation of magnesium should be determined.
- (111) Reasons why hydride prepared by different processes responds differently to surface treatments should be further investigated.
- (1v) An external nucleator system should be developed to provide:
 - a. Better crystals.
 - b. Shorter start-up times.
 - c. Decreased product adhesion and agglomeration.
 - d. Faster feed rates and increased production.
- (v) Techniques to eliminate small amounts of initial gassing in stabilized aluminum hydride should be developed.
- (vi) Determine change, if any, in stabilization derived from various treatments with reduction of storage temperature from 60°C . to 25°C .

[REDACTED]

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Section V

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SECTION VI

(U) GLOSSARY

AP	Ammonium perchlorate
BDNPA	bis(2,2-Dinitropropyl)acetal
DPA	Diphenylacetylene
HX-874	Trifunctional aziridine
2-NDPA	2-Nitrodiphenylamine
LMH-1	Aluminum hydride
NG	Nitroglycerine
PGNC	Plastisol grade nitrocellulose
TEGDN	Triethylene glycol dinitrate
TMETN	Trimethylolethane trinitrate
ZL-437	A polyester resin
FEP Teflon	Polyperfluoroethylenepropylene copolymer
TFE Teflon	Polytetrafluoroethylene

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Security Classification

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1 ORIGINATING ACTIVITY (Corporate author) The Dow Chemical Company Midland, Michigan		2a REPORT SECURITY CLASSIFICATION Confidential
		2b GROUP 4
3 REPORT TITLE High Energy Propellant Ingredient Research and Development		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Annual Technical Summary Report 1 January 1966 - 31 December 1966		
5 AUTHOR(S) (Last name, first name, initial) Brower, F. M.; Daniels, R. D.; Matzek, N. E.; Roberts, C. B.; Snover, J. A.; and Wilson, E. J.		
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8b PROJECT NO. 3148		
8c BPSN Nr. 623148	9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFRPL-TR-67- 38	
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11 SUPPLEMENTARY NOTES		12 SPONSORING MILITARY ACTIVITY AFRPL, RTD Edwards Air Force Base, California
13 ABSTRACT Studies of the preparation and properties of LMH-1 have continued. Stabilizer has been incorporated into product made by the continuous crystallization technique; improved thermal stability is observed in product from the larger unit. Flame photometry is used to determine the equivalence point of the synthesis reaction. Teflon FEP showed excellent promise in the laboratory as a construction material for crystallizer, but adhesion of product still remained a problem in a 9-gallon crystallizer made from FEP stock items. The decomposition mechanism is believed to be the loss of surface hydrogen and formation of nuclei and anion vacancies. Density measurements of continuous and batch stabilized LMH-1 show the formation of a substitutional solid solution. The degree of improvement in thermal stability of "aged," stabilized batch samples of LMH-1 correlates with the initial gassing observed during testing at 60°C. Water, identified as a major component of the gas, plays a major role in the aging process. The decomposition rate of standard LMH-1 in double base propellant at 25°C. became constant at 0.11% per year, requiring 508 days to reach 0.33% decomposition; at 40°C. it reached 0.69% decomposition in 471 days. Double base propellant containing stabilizer-doped, DPA-treated LMH-1 shows a twofold improvement in stability over standard LMH-1 at both 25° and 40°C. Stabilized LMH-1 is remarkably stable at 60°C. Propellant containing "aged" stabilized LMH-1 decomposed 0.74% after 243 days. Other stabilized and treated LMH-1 in double base and composite propellants also show a low degree of decomposition.		

DD FORM 1473

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Light Metal Hydride						
Crystallization						
Stability						
Propellants						
Surveillance						
Manufacturing						

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